CHEMICAL AND MORPHOLOGICAL CHARACTERIZATION OF THE NONCRYSTALLINE FRACTION IN THE HILO SOIL (TYPIC HYDRANDEPTS)

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

AGRONOMY AND SOIL SCIENCE

AUGUST 1972

By

Jenn Kwang Chan

Thesis Committee:

Rollin C. Jones, Chairman
Haruyoshi Ikawa
Ralph Moberly, Jr.

We certify that we have read this thesis and that in our opinion it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Agronomy and Soil Science.

THESIS COMMITTEE

Rollin C. Jones
Chairman

Haruyoshi Ikawa

Nelson Mobley

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF ILLUSTRATIONS

INTRODUCTION

The noncrystalline components are an important constituent in the Hawaiian volcanic ash soils. X-ray diffraction patterns of many Hawaiian soils show a broad amorphous band with very few, if any, crystalline peaks. In this study, the noncrystalline components of a soil include mineral colloids, gels of the oxides of aluminum, iron, and silicon, and associated organic complexes.

Field moisture levels of noncrystalline soils can go as high as 300 percent by weight. Because of their high surface areas, these amorphous fractions can exert considerable influence on the physico-chemical properties of the soils which in turn, strongly influence crop and management practices.

The highly reactive behavior of the noncrystalline components can create problems in soils. For example, noncrystalline materials can immobilize large amounts of phosphorus or can contain high levels of aluminum which can be toxic to plant growth. From the standpoint of ecology, van Olphan (1971) has mentioned that soil pollution can be caused by its ability to sorb pollutants from streams and the atmosphere. Regular use of pesticides and herbicides in cultivated areas can cause drastic accumulations and may upset the soil's biological balance.

So far, characterization of Hawaiian amorphous materials was based primarily on the physico-chemical properties. There is insufficient information pertaining to the chemical-morphological aspects of the soil's amorphous constituents. This present study was designed to add to the knowledge of the chemical-morphological aspects of one

agriculturally important Hawaiian soil, the Hilo series, a member of the Typic Hydrandepts.

The general objectives of this investigation were:

1. Chemical characterization of the noncrystalline component and its volume fraction of selected horizons.
2. Comparative morphological study of the selected soil horizons before and after removal of the noncrystalline phases.

REVIEW OF LITERATURE

In recent years, the study of amorphous materials in soils has aroused considerable interest because their presence has been recognized as having a significant influence on soil physico-chemical properties, some of which are still unknown. Modern instrumentation has facilitated investigations into this highly reactive soil component with enlightening results.

The original concept of allophane as an aluminosilicate (Ross and Kerr, 1934) is still retained although the definition has been modified to include definite SiO_2/Al_2O_3 mole ratios and surface areas (Birrell and Fieldes, 1952; Jackson, 1964a; Swindale, 1965; Yoshinaga, 1966). There is still no consensus among soil researchers as to the most ideal definition of the term "allophane." The term as it appears in the literature has meaning mainly in the perspective of the methods used to characterize the material (McKeague, 1963). A general definition of the term includes any mineral colloid amorphous to x-rays and highly reactive surfaces. This seems vaguely defined because accessory surface amorphous colloids do exhibit similar properties not contained in the definition (Swindale, 1964). Doubts have been expressed by Egawa (1964) on the real nature and structure of allophane and he contends that a chemical procedure to separate "pure allophane" is yet to be established. A tentative definition of allophane was recently proposed by van Olphan (1971) as "members of a series of naturally occurring minerals which are hydrous aluminosilicates of widely varying chemical composition, characterized by short range order, by the presence of Si-O-Al bonds, and by a differential thermal analysis

curve displaying a low temperature endotherm and a high temperature exotherm with no intermediate endotherm."

The noncrystalline material of soils has been referred to as the amorphous hydrated colloidal fraction or the entire range of colloidal materials capable of exhibiting ionic properties except those having true crystalline structure (Sherman et al., 1964). The amorphous fraction of volcanic ash soils in the Pacific region have been widely investigated. A review paper by Kanehiro and Whittig (1961) provides comprehensive coverage on the extent of research on amorphous mineral colloids relevant to the Pacific areas. The role of amorphous fractions of tropical soils was reported by Sherman et al. (1964).

In Hawaii and elsewhere, where amorphous colloidal fractions make up a substantial portion of the soil, a considerable amount of study has been made on the influence of amorphous fractions on agronomic practices and soil management. The high cation exchange capacity of Hawaiian soils, especially Hydrandepts (Hydrol Humic Latosols) was attributed to the high content of amorphous fraction in the soil (Tamura et al., 1953). Marked reduction in the cation exchange capacity occurs on dehydration (Kanehiro and Sherman, 1956). Amorphous materials have also been found in the sea. The mineralogy of amorphous muds in Hawaii (Moberly, 1963) resembled those of the intensely weathered parent source.

Among the Andepts, the Hydrandepts contain the highest amount of amorphous materials. The Akaka soil, a Typic Hydrandept, has been estimated to contain 80 percent amorphous materials (Sherman et al., 1964). The high accumulation of amorphous colloidal fractions has

persisted in the humid areas because it is protected from dehydration (Sherman, 1962). The Typic Hydrandepts which was selected as one of the Hawaiian soils for the investigation on amorphous material colloids by Lai and Swindale (1967) showed the presence of microfibrils and aggregated sponge-like materials in the clay fractions. Tenma (1965) noted that the allophane content decreased with increasing rainfall irrespective of parent material. A greater accumulation of mica, however, occurred in the surface horizons for humid area soils.

The Hilo and Akaka soils are representative of the Typic Hydrandepts that are often selected for soil investigations in Hawaii. A study of both soils from the northeast part of the island of Hawaii indicated that the noncrystalline fractions varied between the two soils and that gibbsite content had a very significant negative correlation with the noncrystalline content (Voss, 1970). From the standpoint of agriculture, the Hilo soil is better suited for sugarcane production than the Akaka soil.

The Typic Hydrandepts, as classified under the new Soil Taxonomy, were formerly known as the Hydrol Humic Latosols. The Hydrandepts belong to the order Inceptisol and have an umbric or an histic epipedon. The umbric epipedon is characterized by an acidic, dark-colored surface horizon, whereas the histic epipedon has a peaty, water saturated horizon (Voss, 1970).

The Typic Hydrandepts from the northeast section of the island of Hawaii are situated in some of the wettest areas of the island. This group of soils is concentrated along the Hilo and Hamakua coasts on the windward slopes of Mauna Kea and Mauna Loa. The mean annual

precipitation can vary from 120 to 200 inches. The parent materials are generally volcanic ash.

Under such humid conditions, these soil are continually wet; thus silica is leached rapidly from the profile. The acid leaching in the presence of much organic matter and reduction of iron compounds in the absence of any pronounced dry season are the probable cause for the lower iron oxide content of this soil group (Tamura et al., 1953). This group of soils has been reported to be composed mainly of gibbsite and amorphous materials.

Distinctive features of these soils are its wetness, smeariness, high water content, low bulk density and irreversible drying. The buffering capacity is known to be high. Kanehiro and Chang (1956) established that there is a direct relationship between buffering capacity and the cation exchange capacity of Hawaiian soils.

The Hilo soil, a member of the thixotropic, isohyperthermic family of Typic Hydrandepts, occur on 10-20 percent slopes at elevations ranging from sea level to 800 feet. This is one of the important soils of the northeastern parts of the island devoted almost entirely to the cultivation of sugarcane for the past hundred years (Voss, 1970). The soil covers an area of about 58,600 acres. The distinct humid conditions had considerably influenced the genesis of this soil thus producing unique qualities which are akin to the Hydrandepts.

The warm, humid conditions under which this soil weathered have produced a mixture of amorphous hydrated colloidal silicon, iron and aluminum oxides and hydroxide gels. Furthermore, air drying of this noncrystalline soil fraction will produce almost pure aggregates of

gibbsite (Sherman et al., 1968). The allophane content of the Hilo soil has been reported to be 30 percent (Tamura et al., 1953) but a recent study of the soil by Voss (1970) indicated little or no allophane based on the silica/alumina ratio. The noncrystalline, allophane-like material was found to be amorphous hydrated aluminum. The high concentration of amorphous material in soils along the Hilo Coast indicates that the composition of the soil fraction is one of the weathering stages in volcanic glass.

The high cation exchange capacity (CEC), high water content, and low bulk density have been attributed to the predominance of amorphous hydrated colloid fractions. Air or oven drying of the moist soil reduces the CEC considerably (Kanehiro and Sherman, 1956) because the hydrated aluminum and iron oxides are converted to inert residues.

The Hilo soil is very responsive to fertilization. The soils have very high capacity to immobilize phosphorus and are very low in total and available potassium (Cline, 1955). Phosphorus solubility and availability in Hilo soils have been reported to be increased by liming (Fox et al., 1962). On the other hand, Rixon (1966) claimed that there was significant increase in CEC with prescribed additions of phosphorus on prelimed Hilo soils.

On the Hilo soil where sugarcane is grown, the use of heavy equipment is carefully controlled. This is due to the thixotropic characteristics of the soil that requires careful soil management. With an adequate fertilization program, this soil seems able to support a major portion of the sugarcane crop on the island of Hawaii.

MATERIALS AND METHODS

Materials

Selection of a Hilo Profile

A profile of the Hilo soil along the Hilo Coast on the island of Hawaii was selected for this study. A morphological description of the profile as well as photographs were taken at the sampling site. Each of the described horizons was sampled and collected separately in double plastic bags and carefully secured to maintain the field moisture conditions.

Description of the Hilo Profile

The Hilo series is a member of the thixotropic, isohyperthermic family of Typic Hydrandepts. It is characterized by a dark brown surface horizon and a yellowish-red to dark-brown epipedon. It has silty clay textures and dehydrates irreversibly.

Pedon: Hilo silty clay loam - sugarcane
(Colors are for moist soil unless otherwise stated)

Ap -- 0 - 16cm -- Dark brown (7.5YR3/2) clay loam; strong fine granules and crumbs; loose, slightly sticky, slightly plastic; many fine roots; many medium and fine pores; pH 4.6; abrupt smooth boundary.

Ap2 -- 16 - 27cm -- Brown (7.5YR4/4) silty clay; moderate medium and coarse prismatic structure breaking to moderate and medium and fine subangular blocky structure; friable, sticky, plastic, slightly smeary, many roots, many fine pores; pH 5.0; clear smooth boundary.

B21 -- 27 - 41cm -- Yellowish red (5YR4/6) silty clay; moderate medium prismatic breaking to strong and medium and fine subangular blocky structure; friable, sticky, plastic, moderately smeary; many roots, many medium and fine pores; pH 5.7; abrupt smooth boundary.

B22 -- 41 - 64cm -- Yellowish red (5YR4/6) gritty silty clay loam; moderate coarse and medium prismatic breaking to moderate medium and fine subangular blocky structure; friable, slightly sticky, plastic; few fine pores, few roots; pH 6.1; clear smooth boundary.

B23 -- 64 - 74cm -- Dark reddish brown (5YR3/4) silty clay; strong coarse and medium prismatic structure breaking to strong, medium and fine subangular blocky structure; friable, sticky, plastic, strongly smeary; few roots; few medium and fine pores; pH 6.2; abrupt smooth boundary.

B24 -- 74 - 81cm -- Dark brown (7.5YR3/2) silty clay and a few fine faint reddish (5YR4/4) mottles; strong coarse and medium prismatic structure breaking to strong coarse medium and fine subangular blocky structure; friable, sticky, plastic, strongly smeary; many fine pores; few roots; pH 6.3; abrupt smooth boundary.

B25 -- 81 - 104cm -- Yellowish red (5YR4/6) silty clay; moderate medium prismatic structure breaking to moderate medium and fine subangular blocky structure; firm, slightly sticky, plastic, strongly smeary; few roots; few fine pores; pH 6.3; abrupt smooth boundary.

B26 -- 104 - 124cm -- Dark reddish brown (5YR3/4) silty clay; strong medium prismatic structure breaking to strong coarse and medium subangular blocky structure; friable, sticky, plastic, slightly smeary, no roots; few medium and fine pores; pH 6.4; abrupt smooth boundary.

B27 -- 124 - 140cm -- Dark brown (10YR4/3) silty clay; strong prismatic structure breaking to strong coarse medium and fine subangular blocky structure; friable sticky and plastic; few roots; many fine and medium pores; pH 6.3.

Methods

Selection of Horizons for Study

X-ray diffraction analysis was carried out on the clay fractions of each horizon using the wet paste method and the auto focusing sample holder. Based on its diffractogram, horizon 7 (B25) was selected because of the broadest amorphous band. Horizon 1 (Ap), most exposed

to weathering forces, was selected for a comparison of differences in mineralogy and noncrystalline fractions.

Preparation of Samples for Analysis

Moisture determination was initially taken for the selected horizons of the profile. The samples were oven-dried at 110°C. Based on their moisture content, sufficient samples from the two horizons were weighed out to undergo hydrogen peroxide treatment in separate 1000 ml beakers at 70°C for five to seven days. The peroxide-treated samples were washed several times with distilled water and then suction-filtered prior to actual chemical treatments. The moisture content of the peroxide-treated samples was determined.

Four 10-gram samples of peroxide-treated and four 10-gram samples of untreated soils were weighed out on an oven dry basis for chemical treatments according to the method of Tweneboah et al. (1967) and a modified procedure using 0.5M HOAc.

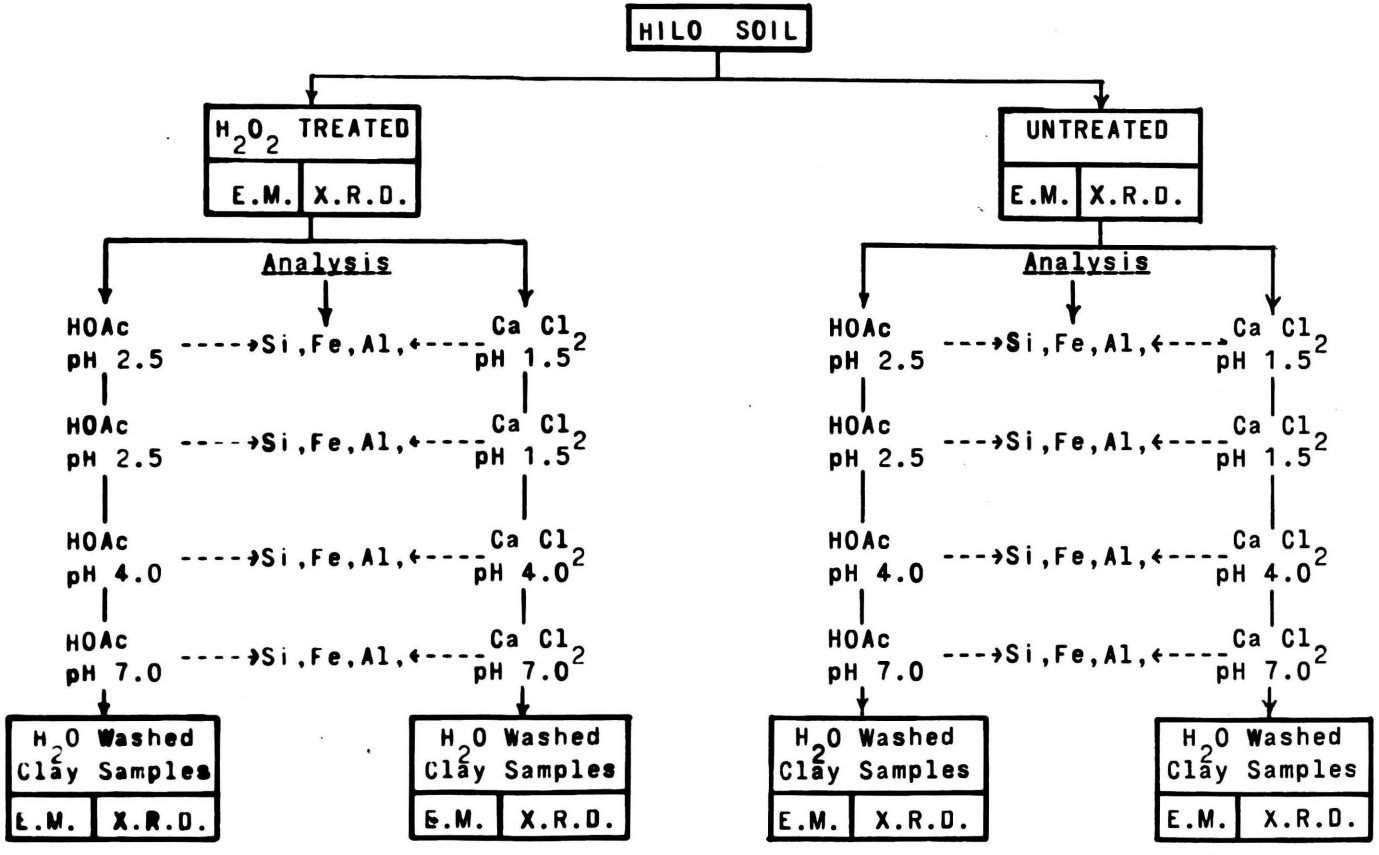
Selective Dissolution of Noncrystalline Fraction

The method of Tweneboah et al. (1967) was slightly modified to remove the amorphous soil constituents in the Hilo soil (hereafter referred to as the Tweneboah method). Similar modifications for use in other Hawaiian soils is reported by Fox et al. (1971). The procedure outlined in the flow diagram in Fig. 1. The method involves two 6-hour continuous agitations of the soil samples with 0.5M $CaCl_2$ at pH 1.5 and subsequent ultrasonic agitations of the samples with 0.5M $CaCl_2$ at pH 4.0 until the supernatant solution was found to be pH 4.0. The sample residues were then shaken for 6 hours with 0.5M $CaCl_2$ at pH 7.0

FIGURE 1

Flow Chart Showing the Procedure of Removing the Non-crystalline Fractions of the Hilo Soil.
(adapted from the method of Tweneboah et al., 1967)

FLOW CHART SHOWING THE PROCEDURE
OF REMOVING THE NONCRYSTALLINE
FRACTIONS OF THE HILO SOIL



E.M.: Electron Microscopy
X.R.D.: X-ray Diffraction

after which they were washed free of any excess salts with distilled water prior to subsequent analysis.

The clay fractions from the treated residue were examined by means of electron microscopy and x-ray diffraction analysis. The solution extracts were saved for the analysis of silicon, aluminum and iron.

A procedure similar to the above (hereafter referred to as the HOAc method), but using 0.5M acetic acid at pH 2.5, pH 4.0, and pH 7.0, was the second treatment to remove amorphous constituents in both peroxide-treated as well as untreated soil samples.

Aliquots of the various supernatant solutions were analyzed immediately for silicon, using the ammonium-molybdate method (Jackson, 1958); for aluminum, using the aluminon-acetate method (Hsu, 1963); and for iron, using the method of Olson (1969). Aluminum and iron were determined by means of a Coleman colorimeter. Silicon was determined with the Bausch and Lomb Spectronic 20 spectrophotometer.

X-ray Diffraction Analysis of Samples

X-ray diffraction patterns of the soil were obtained using a Philips Norelco X-ray diffractometer. A high intensity fine focus tube with a focusing graphite monochrometer was used instead of the conventional nickel-filtered source of radiation. Moist clay fractions were smeared on plastic, fully-focusing holders and scanned at $2^{\circ}2\theta$ per minute.

The clay fractions of peroxide-treated and untreated samples were scanned initially while those that had undergone dissolution treatments were later analyzed after excess salts had been removed.

Electron Microscopy of Samples

The clay fractions from the diluted acqueous suspensions of selected samples were examined by means of a Hitachi HU-11A Electron Microscope operated at 100 KV. Specimens were prepared by collecting a fine mist spray of the suspensions on carbon film substrates. The technique of grid and specimen preparations was described in detail by Jones (1963).

RESULTS AND DISCUSSION

The Approach to the Characterization Study

The chemical and morphological characterization in this study has been based on a comparative study on the treatment effects of two different types of differential dissolution techniques on peroxide-treated as well as untreated soil samples. Chemical analysis of the solution extracts from the two different dissolution treatments was used to estimate the chemical composition as well as to test the effectiveness of each treatment in dissolving the noncrystalline fractions. Further confirmation on each treatment effect was made by means of electron microscopy and x-ray diffraction analysis.

Pretreatments

In the investigation of the soil amorphous fractions, it is desirable to keep chemical pretreatments to a minimum (Mitchell et al., 1964). With pretreatments, soil components under study may run the risk of being chemically altered or destroyed. Pretreatments were inevitable in this study because the removal of organic matter is known to have facilitated the removal of the noncrystalline phase from the crystalline residues using chemical dissolution methods.

Peroxide Treatment

The removal of organic matter has been standard practice in clay mineralogical studies. Organic matter may coagulate, coat, or dilute the soil fraction under investigation. Consequently, it may prevent chemical extractants from reacting with the clay mineral surfaces.

Hydrogen peroxide was used to oxidize the organic matter in this study. The possible mineralogical alteration during the oxidation process has been mentioned by Douglas and Fiessinger (1971) and the formation of soluble and insoluble chelated oxalates of aluminum and iron has been reported by Farmer and Mitchell (1963). Nevertheless, hydrogen peroxide, when judiciously used, is a simple and efficient method in removing that portion of the humus fraction that may interfere with clay mineral analysis. Peroxide treatment has been reported not to have adversely affected the soil inorganic fraction because the hot water extracts of the peroxide treatment showed only traces of silicon, iron and aluminum (Follett et al., 1965).

In this study, the effect of hydrogen peroxide treatment on soils was studied by comparing the x-ray diffraction patterns of samples digested with warm hydrogen peroxide with those receiving no digestion. X-ray diffractograms indicating the effects of hydrogen peroxide treatments showed no apparent change other than a slightly smaller amorphous hump, while electron micrographs showed better dispersion of the noncrystalline samples. After peroxide treatment, the organic matter was found to be 10.3 percent (horizon 1) and 13.7 percent (horizon 7) on an oven-dry basis.

Differential Dissolution

Selective dissolution of the hydrous silica, aluminum and of amorphous aluminosilicates is dependent upon these material having a higher specific surface (giving a higher dissolution rate) than crystalline clays (Jackson, 1964). Since these poorly ordered noncrystalline

fractions occur as coatings on clay surfaces (Jones and Uehara, 1972) or sponge-like gel material, the main approach to estimating their constituents has been to apply chemical degradation procedures by dissolving each of the components selectively. This "cleaning process" allows the clay minerals to be better recognized by means of electron microscopy and to be determined more easily by x-ray diffraction analysis.

The effectiveness of alkali reagents in removing amorphous fractions is objectional from two standpoints:

(1) Incomplete removal, especially the more resistant form of amorphous aluminosilicate (Hashimoto and Jackson, 1960; Mitchell and Farmer, 1962).

(2) Caustic effects on clay minerals using the Hashimoto and Jackson's 0.5N NaOH method (Kawasaki and Aomine, 1965; Sudo, 1954; Jones, 1972).

Support for Tweneboah et al. Method of Selective Dissolution

The method of Tweneboah et al. has been adopted for the removal of the noncrystalline components in this study. This method has been used to remove the noncrystalline coatings from the clay mineral surfaces of several Hawaiian Latosols (Fox et al., 1971). Electron micrographs showed that the treated clay specimens indicated complete removal of the noncrystalline gel hull with no apparent attack on the crystal structures.

Basically, the dissolution of the inorganic constituents of the noncrystalline components are based on the mobility of the cations under the influence of predetermined pH levels. A series of solubility

curves of the principal amorphous components of weathering silicate minerals compiled by Loughnan (1969) were used as a source of reference on the solubility of the noncrystalline fractions based on pH levels (See Fig. 2).

Tweneboah method is a selective acid extraction of "active" aluminum and iron from oxides and clay minerals using 0.5M $CaCl_2$ as an extractant at pH 1.5, 5.0, 7.0. In their original study, Tweneboah et al. (1967) also determined the charge characteristics of a number of soils simultaneously. One of the merits cited out by the authors for this dissolution technique was the limited possibility of the interaction and precipitation of silicon and aluminum at low pH.

Effects of Dissolution Treatment

The silicon, aluminum and iron in the noncrystalline fractions were removed in variable amounts from the peroxide-treated and untreated samples from horizons 1 and 7. Generally, greater amounts of silicon and aluminum were removed from the peroxide-treated samples. However, less iron was removed from the peroxide-treated than from the untreated samples. A higher extraction of the constituents might imply greater efficiency in the dissolution process without the partial inhibitory effects of organic matter. This superior trend was later substantiated by improved x-ray diffractograms of clay samples that underwent similar treatments.

The overall chemical data indicate a rapid release of silicon and aluminum in all samples at pH 1.5 or 2.5 of the two extractants. The low Si/Al ratios obtained during the initial two extractions in this

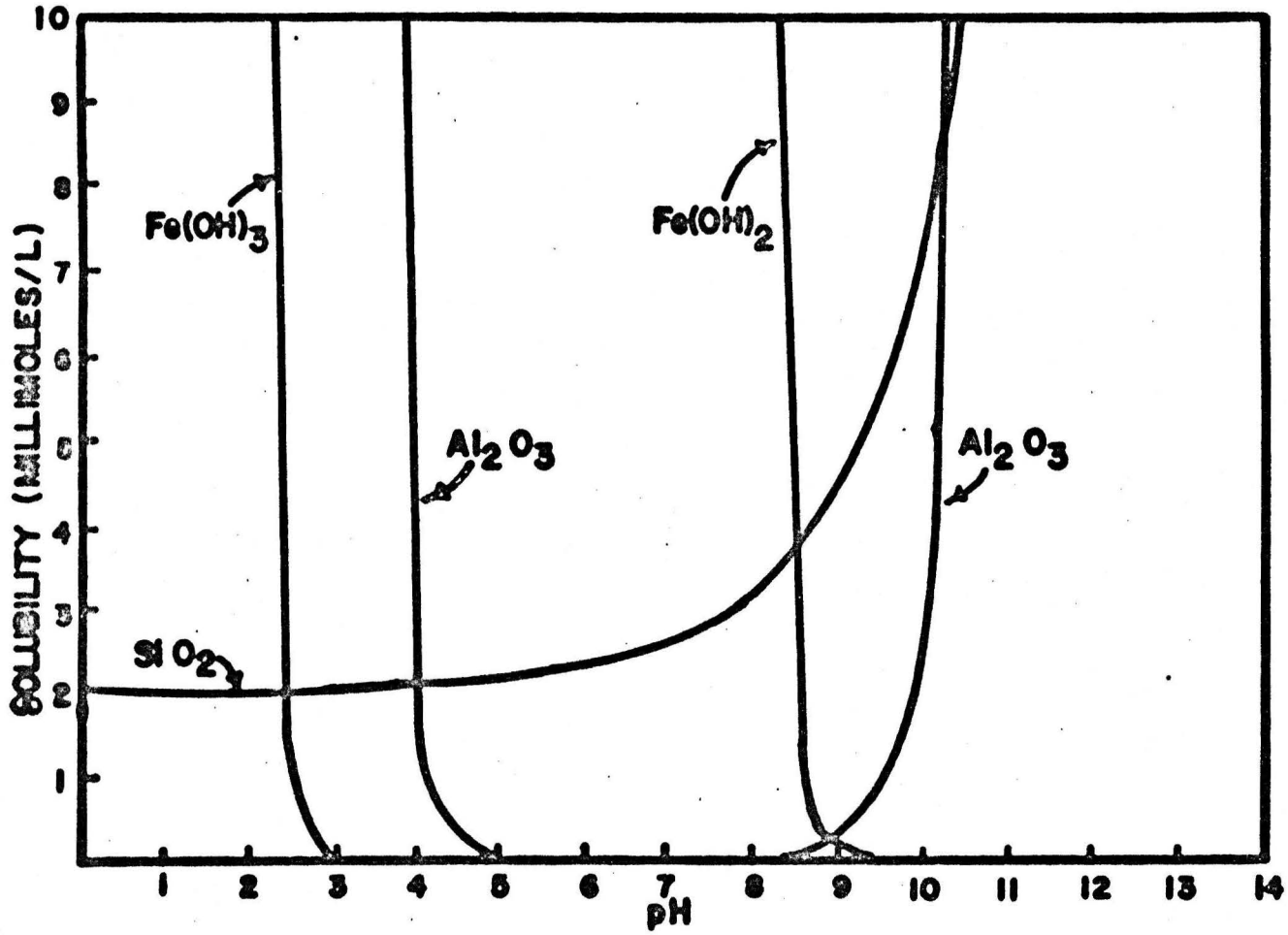


FIGURE 2

The Solubility of Major Amorphous Components based on pH.
(after Loughnan, 1969)

study showed similar trends as those found by Tweneboah et al. in their study. They attributed their low initial Si/Al ratios of their extracts to the dissolution of a form of oxide that is more soluble than the crystalline particles.

The Solubility of Major Amorphous Constituents

Silicon

Amorphous silica is known to be ten times more soluble than quartz (Correns, 1969). The solubility of silica is governed not only by pH levels but also by temperature variations (Morey et al., 1964). Iron and aluminum oxides also decreased silica solubility (Jones and Handreck, 1963). Particle size and the degree of crystallinity are other factors also involved in silica solubility. Based on the chemical data (See Tables 1 and 2), it was evident that more silica was solubilized at pH 1.5 or 2.5 for the two extractants. The high initial solubility may be due to the large surface areas reacting with the extractants and to the amorphous silica being relatively more soluble than the other crystalline components. Remnants of the amorphous silica were removed at pH 4.0, while hardly any silica were removed at pH 7.0.

In this study, silica removal with respect to pH, does not agree with that of Correns (1949) who postulated that amorphous silica solubilizes increasingly from pH 2 to 11. Perhaps the idea of Correns must be viewed with caution because recent findings seemed to discount such trends (McKeague and Cline, 1963).

Table 1. Soluble noncrystalline fractions extracted from horizon 1 of the Hilo soil.*

0.5 M $CaCl_2$ (Tweneboah Method)								0.5 M HOAc (HOAc Method)							
Untreated				Peroxide-treated				Untreated				Peroxide-treated			
pH	Si	Al	Fe	pH	Si	Al	Fe	pH	Si	Al	Fe	pH	Si	Al	Fe
1.5	0.49	1.31	0.53	1.5	0.80	2.18	0.19	2.5	0.06	0.30	0.01	2.5	0.60	1.78	0.11
1.5	0.29	0.64	0.78	1.5	0.35	1.24	0.54	2.5	0.07	0.26	0.02	2.5	0.20	0.83	0.11
4.0	0.13	0.27	0.02	4.0	0.10	0.18	0.01	4.0	0.07	0.13	0	4.0	0.04	0.07	0.01
7.0	0.01	0.01	0	7.0	0.02	0.04	0	7.0	0	0	0	7.0	0.04	0.04	0
Total	0.92	2.23	1.33	Total	1.27	3.64	0.74	Total	0.20	0.69	0.03	Total	0.88	2.72	0.23
	SiO_2	Al_2O_3	Fe_2O_3		SiO_2	Al_2O_3	Fe_2O_3		SiO_2	Al_2O_3	Fe_2O_3		SiO_2	Al_2O_3	Fe_2O_3
	1.97	4.21	1.90		2.72	6.88	1.06		0.43	1.30	0.04		1.88	5.14	0.33
$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$			0.6188				0.6108				0.5503				0.5973

*Results are expressed as percentage of original soil before dissolution treatments.

Table 2. Soluble noncrystalline fractions extracted from horizon 7 of the Hilo soil.*

0.5 M $CaCl_2$ (Tweneboah Method)								0.5 M HOAc (HOAc Method)							
Untreated				Peroxide-treated				Untreated				Peroxide-treated			
pH	Si	Al	Fe	pH	Si	Al	Fe	pH	Si	Al	Fe	pH	Si	Al	Fe
1.5	0.24	0.64	0.39	1.5	0.48	1.19	0.15	2.5	0.05	0.20	0.01	2.5	0.37	0.49	0.15
1.5	0.14	0.33	0.82	1.5	0.15	0.49	0.77	2.5	0.06	0.15	0.02	2.5	0.10	0.61	0.15
4.0	0.04	0.12	0.02	4.0	0.04	0.09	0.01	4.0	0.05	0.10	0.01	2.5	0.02	0.07	0.02
7.0	0.01	0	0	7.0	0.01	0	0	7.0	0	0	0	7.0	0	0	0
Total	0.43	1.09	1.23	Total	0.68	1.77	0.93	Total	0.16	0.45	0.04	Total	0.49	1.17	0.32
	SiO_2	Al_2O_3	Fe_2O_3		SiO_2	Al_2O_3	Fe_2O_3		SiO_2	Al_2O_3	Fe_2O_3		SiO_2	Al_2O_3	Fe_2O_3
	0.92	2.06	1.76		1.46	3.35	1.33		0.34	0.85	0.06		1.05	2.21	0.46
$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$			0.4903				0.5912				0.6511				0.7172

*Results are expressed as percentage of original soil before dissolution treatments.

Iron

Amorphous ferric oxides as well as discrete particles occur as surface coatings on minerals. Ferric oxides were claimed to be a significant constituent in the heterogeneous mixture of amorphous soil materials including allophane (Mitchell et al., 1964; Jackson, 1956; Sherman et al., 1964). Deferration processes, prior to mineralogical analysis, simultaneously remove considerable amounts of silicon and aluminum from soils containing large amounts of disordered alumino-silicates which might indicate that ferric compounds are intimately mixed with the rest of the amorphous compounds (Mitchell et al., 1964; Follett et al., 1965).

Amorphous iron oxides have been removed from crystalline materials by means of ammonium oxalate at pH 3.0 (Schwertmann, 1959). "Yellow ochre" consisting mainly of amorphous iron oxide and goethite were also removed by means of sodium dithionite ($Na_2S_2O_4$) at pH 3.3 (Mitchell and Mackenzie, 1959).

The mobility of $Fe(OH)_3$ is pH-dependent (Loughnan, 1969). Tables 1 and 2 showed that the initial pH of 1.5 for $CaCl_2$ (Tweneboah method) effectively removed considerable amounts of iron oxides. In most cases, there was more iron removed during the second acid extraction indicating that more iron had been mobilized. Insignificant amounts were removed at pH 4.0 while none at pH 7.0. The greater amounts of iron extracted from the untreated samples may have been contributed by the iron solubilized from the organo-clay complex fractions at pH 1.5. It is possible that during the oxidation process, the ferrous forms may have been converted to the insoluble ferric forms which

would not have been detected during analysis.

Aluminum

The solubility of aluminum is highly dependent on pH. According to the solubility curves of Loughnan, aluminum is soluble at two pH ranges, one on the alkaline range above pH 10 and the other in the acid range between 4.0 and 4.5. Loughnan (1969) mentioned that both amorphous aluminum and gibbsite appear to have a marked affinity for silicon. This would suggest the lack of amorphous aluminum in soils because it is stabilized with silica in allophane (Rich and Thomas, 1960).

Aluminum was extracted in greater amounts than silicon or iron in this study (See Tables 1 and 2). Tweneboah et al. has mentioned that aluminum can best be extracted around pH 1-1.5 with a minimal dissolution of iron in their original study. The rapid dissolution of aluminum at this pH range suggests that there is a more soluble, active form of an oxide being solubilized.

Selective Dissolution Using 0.5M Acetic Acid

The HOAc dissolution method was used to determine the effectiveness of the removal of amorphous materials with 0.5M acetic acid (HOAc). This method is based on the solubility characteristics of amorphous iron and aluminum as related to pH values as reported by Loughnan (1969). Similarly, it was thought that by substituting another acid-dissolution system with almost similar pH values, equal effects could be achieved by the treatments.

The use of HOAc as a possible substitute extractant were based on

the assumption that:

(1) It was a mild acid that may not alter the character of the clay minerals during the dissolution treatment.

(2) Stable pH could be maintained by using a buffered-acetate system during the dissolution process.

Ostrom (1961) used HOAc to extract clay minerals from carbonate sediments. He found that the HOAc could affect mineral structure depending on the reagent concentration and the degree of crystallinity of the clay minerals.

0.5 Mole HOAc has an initial pH of 2.58. Based on Loughnan's solubility curves, this pH level is still practical for removing $Fe(OH)_3$. The results of the 0.5M HOAc dissolution treatments on peroxide-treated and untreated soil samples indicate that silicon, aluminum and iron were removed in greater amounts from the former samples. The overall performance of the HOAc treatments, based on chemical analysis of the extracts, indicated that the noncrystalline fractions have not been dissolved to the same extent as that solubilized by the Tweneboah method. The HOAc treated residues did not show x-ray diffraction peaks as intense as those after the Tweneboah method. There were no significant differences between the effects of the two dissolution techniques of organic matter-free clay specimens as observed from the electron micrographs.

Effects of Organic Matter on the Removal of Noncrystalline Fractions

The humus fraction of soil organic matter is composed of highly reactive compounds capable of forming organo-clay complexes. Allophane soils have Ch/Cf (humic acid/fulvic acid) ratio ranging from 0.3-1.3

(Tokudome and Kanno, 1965). These organic colloids are thought to occur on the surfaces of inorganic particles or the surface of silicic acid gels through hydrogen bonding (Russell, 1961). Humus is able to chelate di-, tri-valent cations fairly tenaciously and form insoluble metal complexes.

The removal of organic matter definitely had beneficial effects on the dissolution of the noncrystalline fractions; x-ray diffraction patterns and electron micrographs reflect this also. The presence of organic matter coagulates or coats the soil particles which may make chemical dissolution less effective. The lower extractions of silicon and aluminum in the untreated soil samples seemed to be influenced by the numerous complex behavior of humus in the soil (with the exception of the high iron extraction by the Tweneboah method (See Tables 1 and 2). One possible hypothesis for the lowered extraction of peroxide-treated samples may be due to iron complex formations.

Similar results were found by Oades and Townsend (1963). They showed that iron was complexed during the oxidation of soil organic matter by hydrogen peroxide. This behavior was presumably influenced by acidic groupings produced during the oxidative breakdown of the organic matter.

X-Ray Diffraction Analysis (XRD)

A preliminary analysis of moist whole clay fraction from each horizon of the Hilo soil was made to ascertain the overall mineralogical composition of the selected profile. The diffraction patterns of randomly oriented clay specimens of the 9 horizons indicated the pre-

dominance of x-ray amorphous materials (See Fig. 3). Diffraction peaks at 4.15A, 3.32A and 2.42A in four subhorizons indicate the presence of small amounts of goethite, quartz and magnetite, respectively.

The clay fractions of peroxide treated and untreated soil specimens from the selected horizons (hereafter referred to as horizon 1 and 7) were analyzed by XRD to determine if there were differences in the diffractograms as a result of organic matter removal using hydrogen peroxide.

As mentioned previously, there were no significant differences between the diffractograms between the peroxide treated and untreated clay fractions except for a slight lowering of the amorphous band. Oxidation of organic matter using hydrogen peroxide has been known to degrade clay minerals (Douglas and Fiessinger, 1971). It was thought that low pH level of the slurry during the peroxidation process was responsible for the mineral degradation and a buffered system was recommended. In this study, there was no discernible alteration of the mineralogy detected by x-ray diffraction because of the predominance of amorphous bands.

Effects of Treatments

Peroxide treated and untreated clay size residues were analyzed by XRD after the Tweneboah and HOAc methods. The removal of the amorphous fraction from the samples was indicated by the virtual disappearance of the broad amorphous band and an enhancement of diffraction peaks as a result of concentrating the crystalline fractions present (See Fig. 4 and 5).

Based on the results of the eight treatments, it was evident that

FIGURE 3

X-ray Diffraction Patterns of the Hilo Soil Horizons to Show the General Amorphous Nature of the Soil. ($Cu\text{-}K_{\alpha}$)

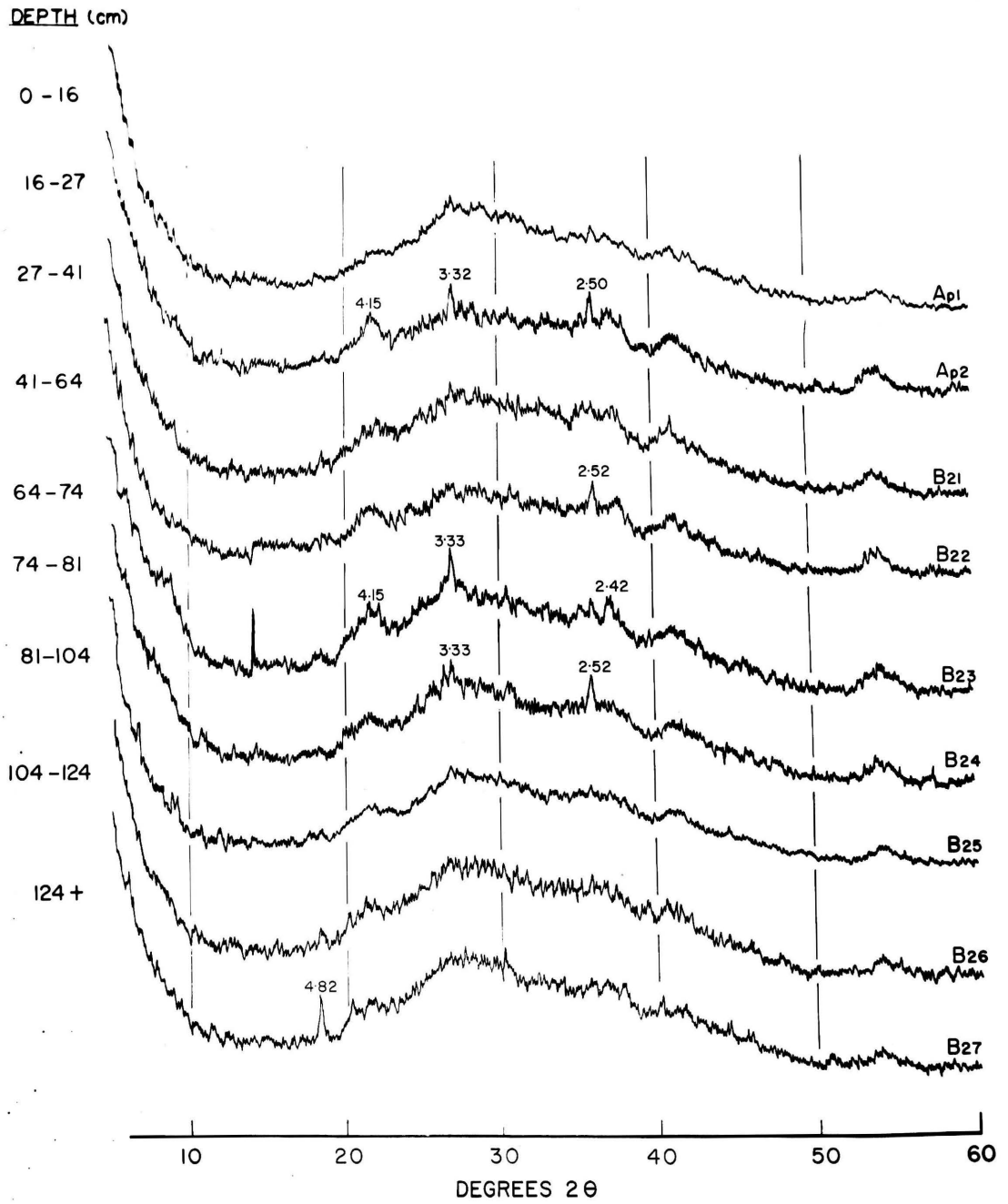

DEPTH (cm)
0 - 16
16 - 27
27 - 41
41 - 64
64 - 74
74 - 81
81 - 104
104 - 124
124 +
4·15
3·32
2·50
Ap1
Ap2
2·52
B21
B22
3·33
4·15
2·42
B23
3·33
2·52
B24
B25
B26
4·82
B27
10
20
30
40
50
60
DEGREES 2θ

FIGURE 4

X-ray Diffraction Patterns of the Clay Size Fractions of Horizon 1 of the Hilo Soil Shwoing the Effects of Treatment by the Tweneboah et al. Method
I. Untreated II. Peroxide-treated
A. After Differential Dissolution Treatments
B. Before Differential Dissolution Treatments
(Cu-K_{α})

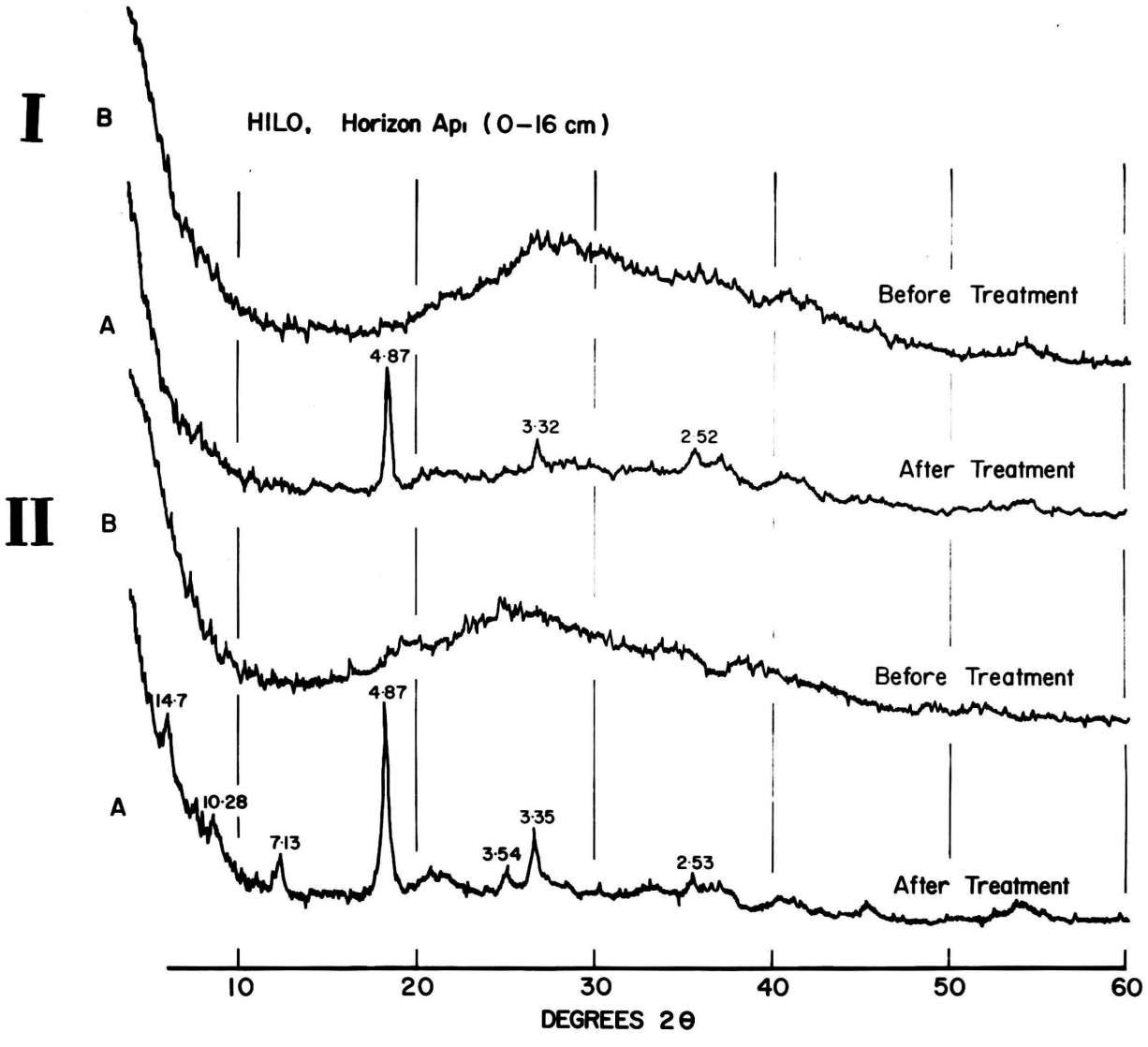
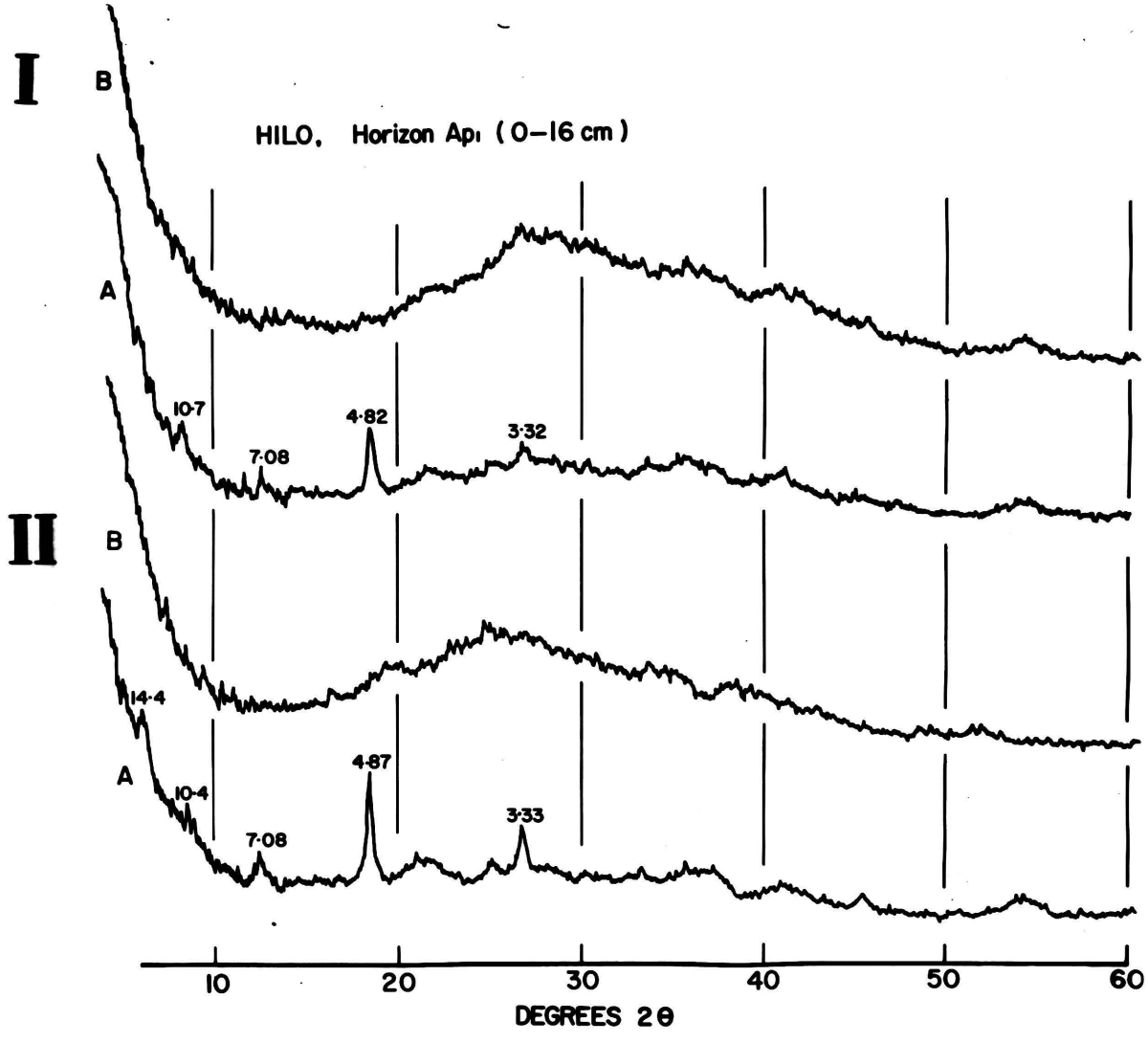

I
B
HILO, Horizon Ap1 (0–16 cm)
A
Before Treatment
4·87
3·32
2·52
After Treatment
II
B
Before Treatment
14·7
4·87
A
10·28
3·35
7·13
3·54
2·53
After Treatment
10
20
30
40
50
60
DEGREES 2θ

FIGURE 5

X-ray Diffraction Patterns of the Clay Size Fractions of Horizon 1 of the Hilo Soil Shwoing the Effects of Treatment by the HOAc Method
I. Untreated II. Peroxide-treated
A. After Differential Dissolution Treatments
B. Before Differential Dissolution Treatments
($Cu\text{-}K_{\alpha}$)


I
B
HILO, Horizon Ap1 (0–16 cm)
A
10·7
7·08
4·82
3·32
II
B
14·4
A
10·4
7·08
4·87
3·33
10
20
30
40
50
60
DEGREES 2θ

organic matter-free samples revealed sharp crystalline peaks after differential dissolution treatments. Peroxide-treated clay fractions that had undergone Tweneboah et al. treatment appear to have the greatest amount of the amorphous materials removed. This was evidenced by a marked improvement in the diffraction pattern as shown by higher peak intensities and lesser background scatter. The clay fraction of the untreated samples probably contained high amounts of humus and organic colloids that rendered the amorphous fractions resistant to the dissolution process. Because of this, remnants of the amorphous materials in the soils after dissolution treatments may have obscured the full appearance of crystalline diffraction peaks by their dilution effect.

Apart from variations in amorphous content after the overall treatments, the mineralogy of horizon 1 and 7 appeared to be similar. Voss (1970) detected 10A and 7A peaks in diffractograms of lower horizons of the Hilo soil but minerals associated with these peaks were not identified by him. The vermiculite-chlorite integrades and imogolite have been reported to possess similar peaks (Kawasaki and Aomine, 1965). The frequent occurrence of peaks around 14A, 10A, and 7A in this investigation may suggest similar chloritic minerals and the presence of imogolite. The occurrence of imogolite has been confirmed by electron microscopy. The remaining crystalline minerals of any significance were gibbsite, kaolinite, quartz, and magnetite. Gibbsite with a diffraction maxima generally at 4.82A appeared in all diffraction patterns that had undergone overall differential chemical treatments. Kaolinite with a diffraction maxima at 7.13A appeared in diffraction

patterns of peroxide-treated clay specimens of horizons 1 and 7 that had undergone both the Tweneboah and HOAc methods. The 7.08A peak may be the second order peak of the undefined 14A peak. Quartz with a maxima at approximately 3.33A and magnetite with a maxima at 2.52 occurred in the diffractograms of the peroxide-treated and untreated clay that had undergone the respective dissolution treatments (See Fig. 4 - 7).

It may be difficult to indicate which of the two horizons had greater amounts of amorphous materials based just on x-ray diffraction patterns alone. The chemical analysis shows that more soluble amorphous materials have been extracted from horizon 1 than horizon 7. This could be exemplified by the diffraction patterns of peroxide-treated clay fractions that underwent the Tweneboah treatment from horizon 7. A slight amorphous band still appeared in the diffractogram and may indicate an incomplete removal of the amorphous materials from that horizon.

Electron Microscopy

The use of electron microscopy was complementary to chemical and x-ray diffraction techniques in studying the morphology of the non-crystalline components of the Hilo soil. Electron microscopy was used to follow any morphological changes which may have occurred as a result of the various treatments. The results indicated that the main constituents of the soil consisted primarily of noncrystalline materials with minor amounts of crystalline minerals.

FIGURE 6

X-ray Diffraction Patterns of the Clay Size Fractions of Horizon 7 of the Hilo Soil Showing the Effects of Treatment by the Tweneboah et al. Method
I. Untreated II. Peroxide-treated
A. After Differential Dissolution Treatments
B. Before Differential Dissolution Treatments
($Cu\text{-}K_{\alpha}$)

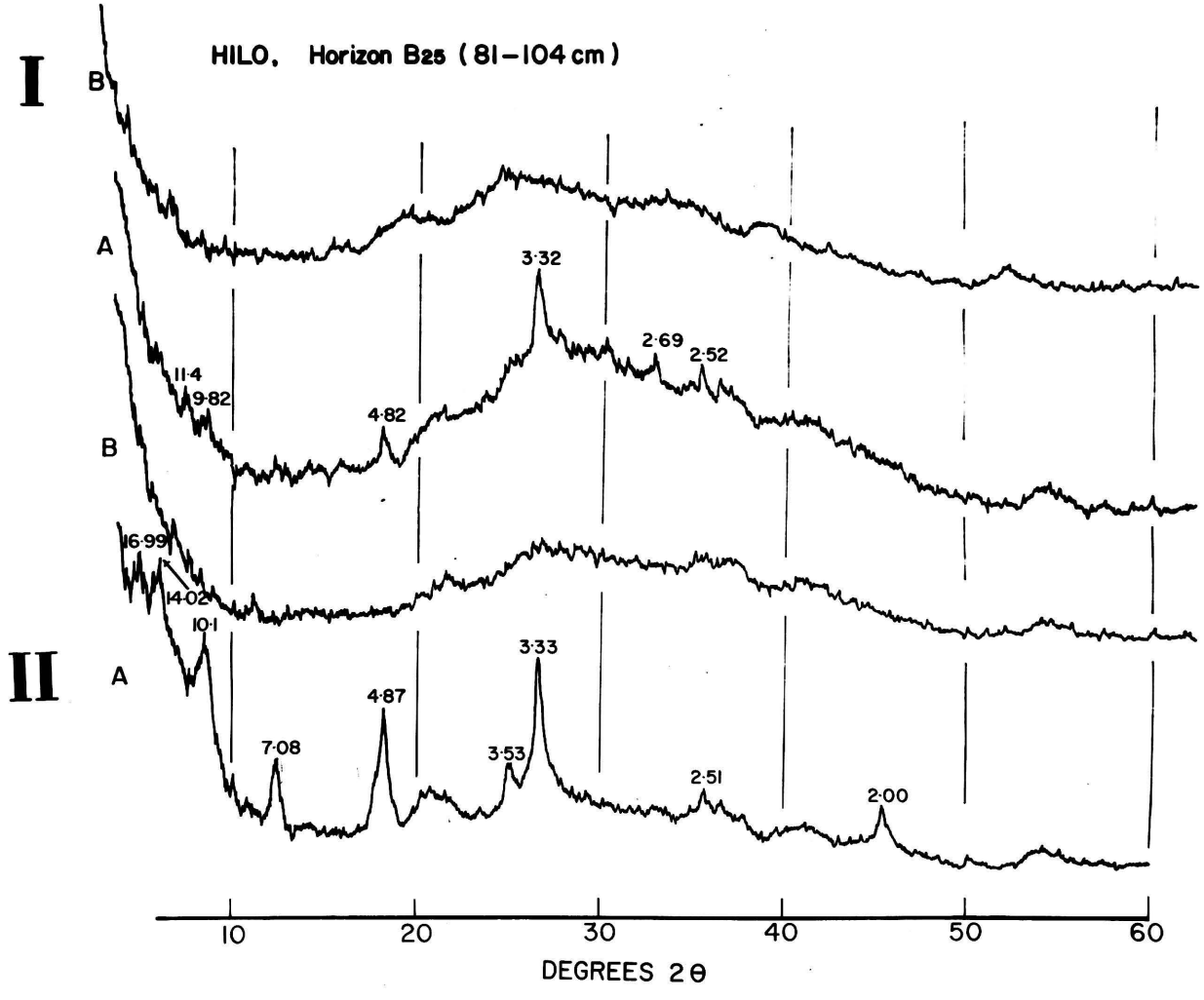
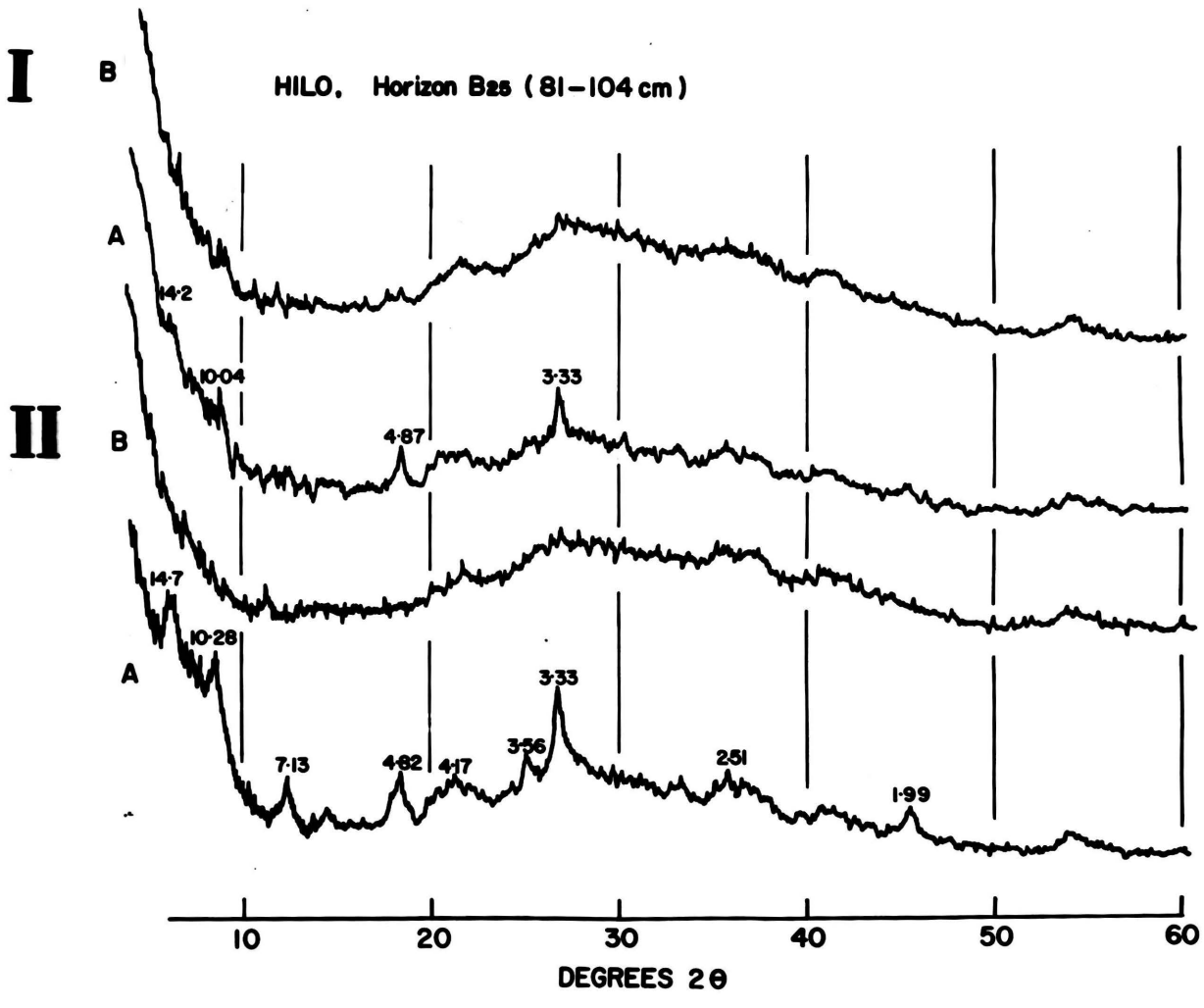

I
HILO, Horizon B25 (81–104 cm)
B
A
B
II
A
3·32
2·69
2·52
11·4
9·82
4·82
16·99
14·02
10·1
3·33
4·87
7·08
3·53
2·51
2·00
10
20
30
40
50
60
DEGREES 2θ

FIGURE 7

X-ray Diffraction Patterns of the Clay Size Fractions of Horizon 7 of the Hilo Soil Showing the Effects of Treatments by the HOAc Method
I. Untreated II. Peroxide-treated
A. After Differential Dissolution Treatments
B. Before Differential Dissolution Treatments
(Cu-K_{α})


I
B
HILO, Horizon Bss (81–104 cm)
A
14·2
II
10·04
4·87
3·33
B
14·7
10·28
A
3·33
7·13
4·82
4·17
3·56
2·51
1·99
10
20
30
40
50
60
DEGREES 2θ

Noncrystalline Components

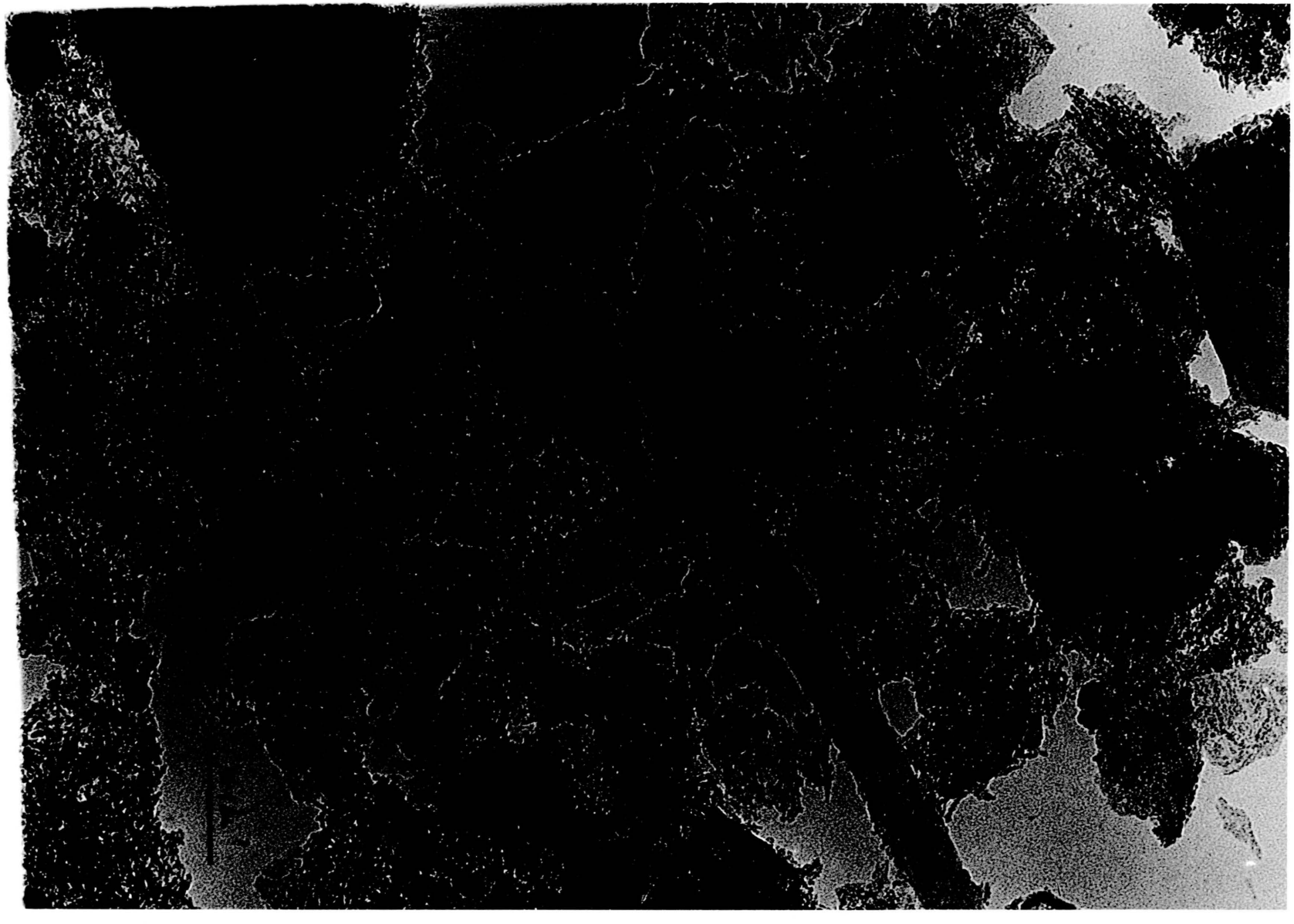
A notable feature of the noncrystalline component was that it lacked structural organization (Plate I). The principal constituents of the amorphous inorganic materials are the oxides, or more usually, the hydrous oxides of iron, silicon, manganese and other organo-mineral complexes (Mitchell et al., 1964). In this study, no attempt was made to isolate the individual components of this highly complex amorphous mixture for morphological studies, but instead, they were collectively regarded as noncrystalline components.

"Allophane" has been a popular term to mean the amorphous fraction extracted from the soil using alkali reagents such as NaOH or Na_2CO_3 after deferration pretreatments. The morphology of allophane and related mineraloids has been reported to be diverse (Wada, 1967). This diversity has been attributed to differences in the exact nature of the specimens examined, dispersion techniques, pretreatment and mounting procedures. Inorganic amorphous admixtures of silicon, iron and aluminum have been described as transparent, aggregated, globular particles with fluffy appearance (van Der Marel and Beutelspacher, 1968). However, this description also seems appropriate for allophane which is described as being composed of only silicon and aluminum and water.

Because of the many inconsistencies in the definition and description of allophane, it is felt that the term "noncrystalline" was more appropriate for use in this study. Electron microscopy studies of the noncrystalline materials in this study have shown it to be comprised of translucent gels, short and thickened, strand aggregates and elongated,

PLATE I

Electron Micrograph at Low Magnification Showing the General Morphology of the Clay Size Fractions of the Hilo Soil. It is comprised of different forms of noncrystalline components
(Magnification: X 220,000)



fibrous imogolite (Plates II - IV).

The translucent gels usually occur as coatings on mineral surfaces, as electron opaque particulates and as filmy gel masses. These sponge-like aggregates appear to be composed of minute spherical particles connected by fine filaments when viewed at high magnifications.

Within the dense mass of gel material, there often occur short, densely weaved, spingle-shaped particulates. These particulates appear to coexist with the gel fractions as thick masses with no preferential orientation. They seem to be resistant to separation even after ultrasonication and differential dissolution treatments (Plate III). Working with a soil closely related to the Hilo series, Lai (1967) has postulated that the network of fibrous material will gradually form sponge-like flakes which will finally transform into plate-like crystals. Closely meshed fibrous materials were also detected on electron micrographs of the clay size specimens although no plate-like crystals at the various stages of transformation were ever recognized. This author is of the opinion that the closely meshed fibrous bundles (See Plate V) are the skeletal remains of highly weathered feldspar, pyroxene or olivine. If skeletal material is the remains of feldspar, it may be primarily composed of $SiO_2 \cdot Al_2O_3$; the bases having been weathered away. However, the most plausible explanation of the skeletal material is that it is primarily Fe_2O_3, left after silicon and magnesium have been weathered out from olivine or pyroxene. This idea is supported by the high electron opacity of the individual spleroids making up the skeleton. On the other hand, the good electron transmission between the spheroids indicates the open nature of the skeleton.

PLATE II

Electron Micrograph Showing the Fluffy, Gel-like Mass Which is One of the Major Noncrystalline Components of the Hilo Soil. The Gel-like mass appear to be composed of aggregated, minute, spherical particulates that seemed to co-exist with imogolite.
(Magnification: X 80,000)

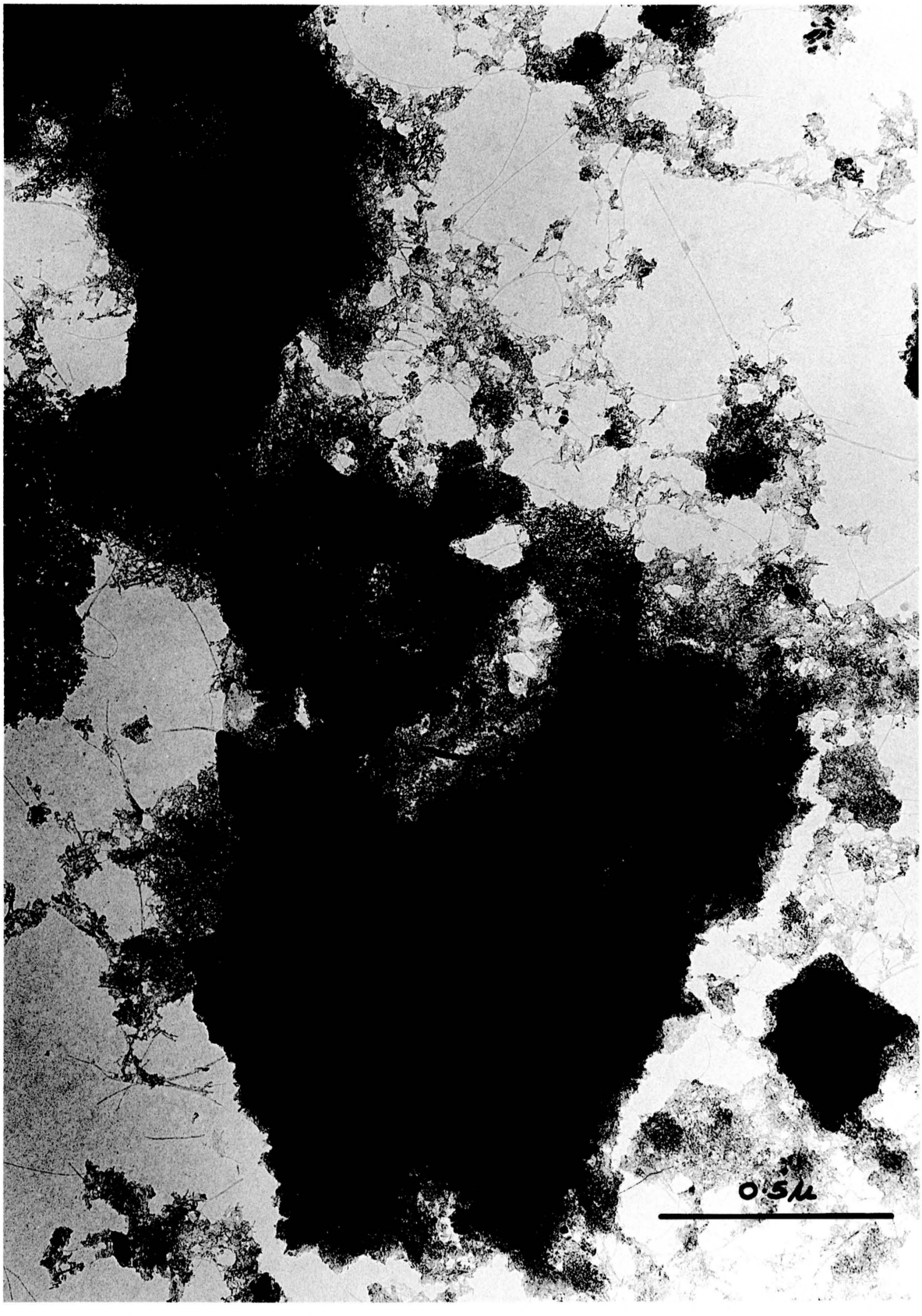

0.5μ

PLATE III

Electron Micrograph Showing the Densely Woven, Short, Thickened Spindle-shaped Units Which are the Major Noncrystalline Components of the Hilo Soil. The units within these irregular masses were resistant to separation even after prolonged sonication. (Magnification: X 250,000)

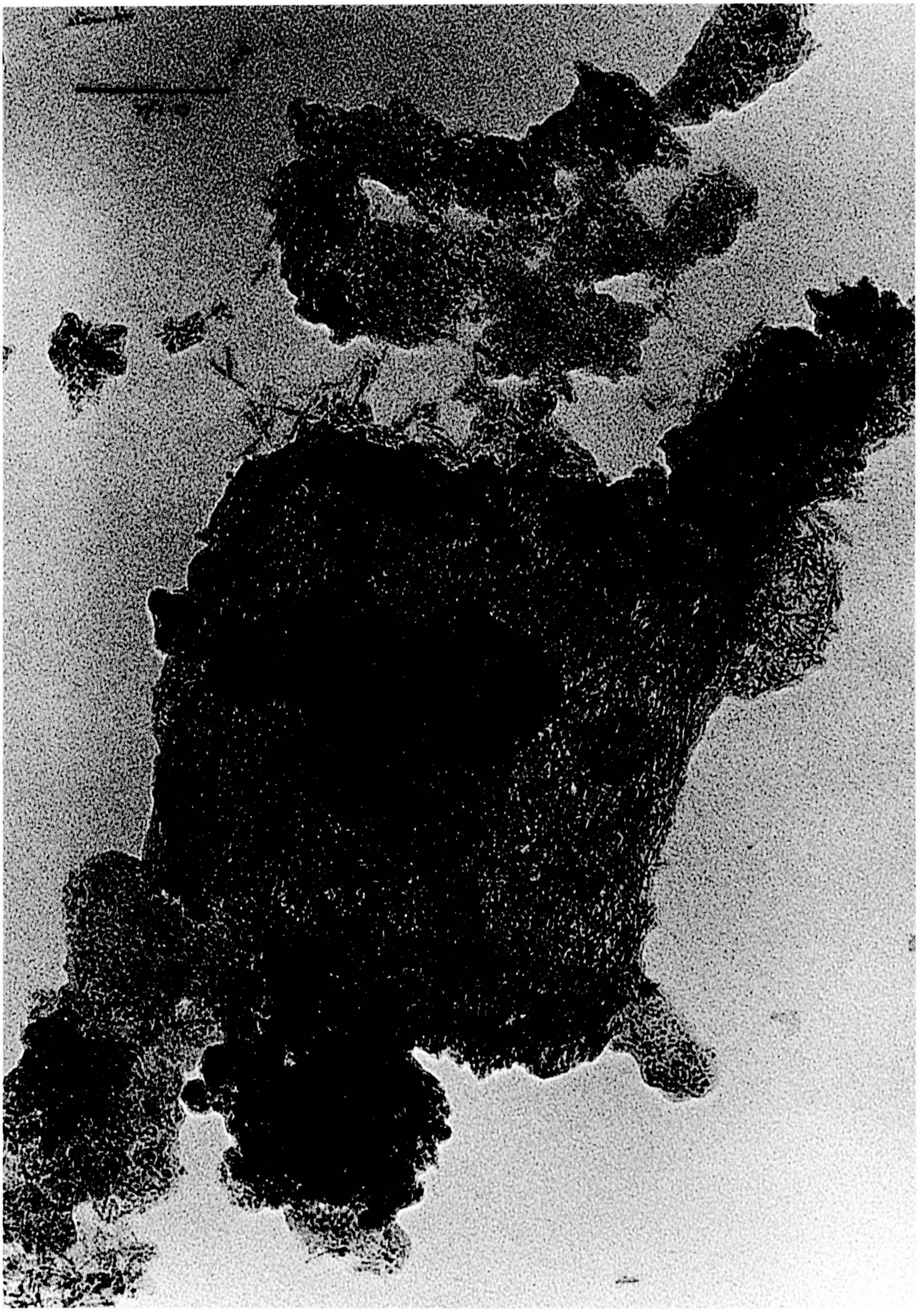
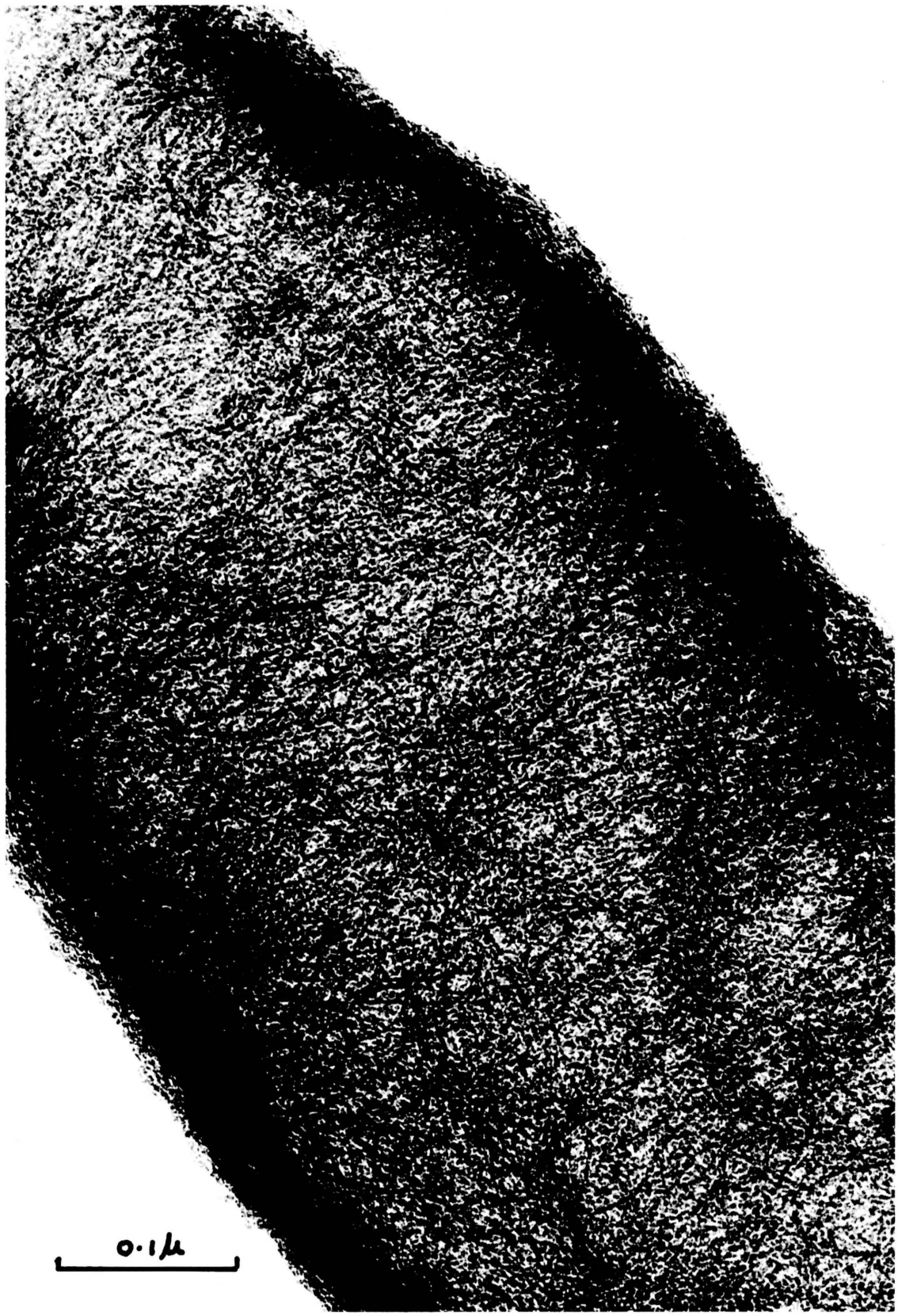


PLATE IV

Electron Micrograph Showing the Fibrous Morphology of an Isolated Bundle of Imogolite. The individual strands were intertwined within the fibrous mass. Imogolite were considered to be one of the major components of the noncrystalline fractions of the Hilo soil. (Magnification: X 300,000)

PLATE V

Electron Micrograph at High Magnification Showing the Skeletal Remains of Highly Weathered Feldspar of the Hilo Soil. The high opacity of the individual spheroids making up the skeleton were thought to be primarily Fe_2O_3.
(Magnification: X 300,000)


0·1μ

Imogolite, the extremely fine, slender, hair-like particles often occurred in most clay specimens whether they underwent chemical dissolution techniques or not. These discrete particles coexist intimately with the gel materials and can individually be separated into their own components (Yoshinaga and Aomine, 1962). Imogolite has been established to be more structurally organized than the amorphous fractions by Wada (1967). He has hypothesized the crystalline structure to be a chain-shaped structural unit. It has also been demonstrated that imogolite can be loosened from the gel-like film by strong sonic waves (Miyauchi and Aomine, 1966). Because of its low crystallinity, imogolite is regarded by the author as a component of the noncrystalline fractions of the Hilo soil.

The morphology of the imogolite of the Hilo soil resembles those general features established by the Japanese soil researchers. Electron micrographs of untreated samples indicated that imogolite tends to form interconnecting strands between denser aggregated noncrystalline aggregates (Plate VI). These slender strands appear fairly uniform and measure 15 to 20A in diameter (Plate VII). Yoshinaga et al. (1970) reported the external measurements of individual strands to be 17 to 21A. The actual length of the individual fibers has not been determined although some measure several microns long. Russell et al. (1969) have reported that imogolite is susceptible to partial dissolution by alkali reagents as evidenced by the finer appearances of the fibers after the final separation process. It is essential, therefore, to minimize pretreatments before final analysis so that valid diameter measurements can be made.

PLATE VI

Electron Micrograph at Low Magnification Showing the Interconnecting Characteristics of Imogolite Strands of the Untreated, Horizon 1 Clay Size Fractions from the Hilo Soil.
(Magnification: X 110,000)

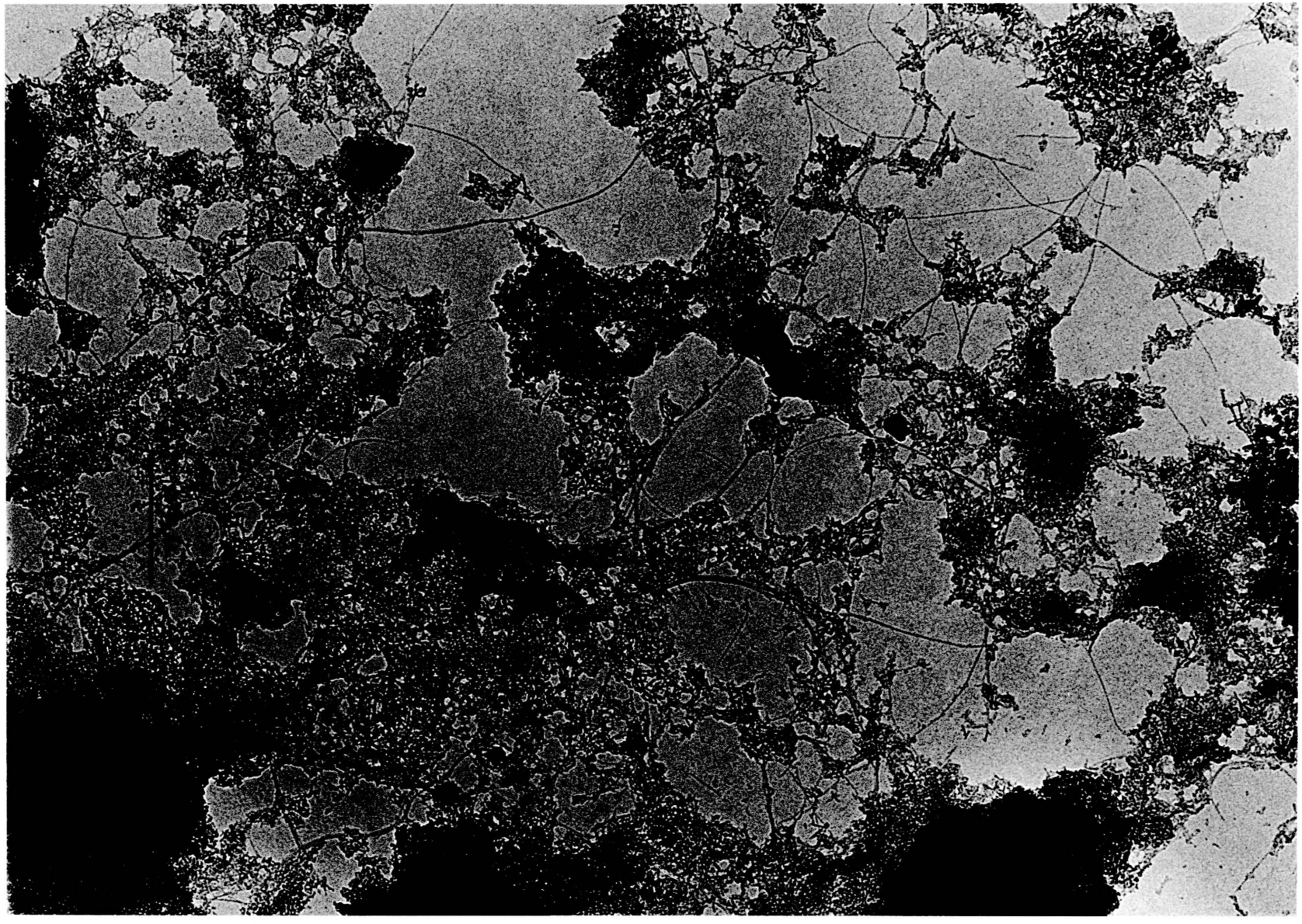
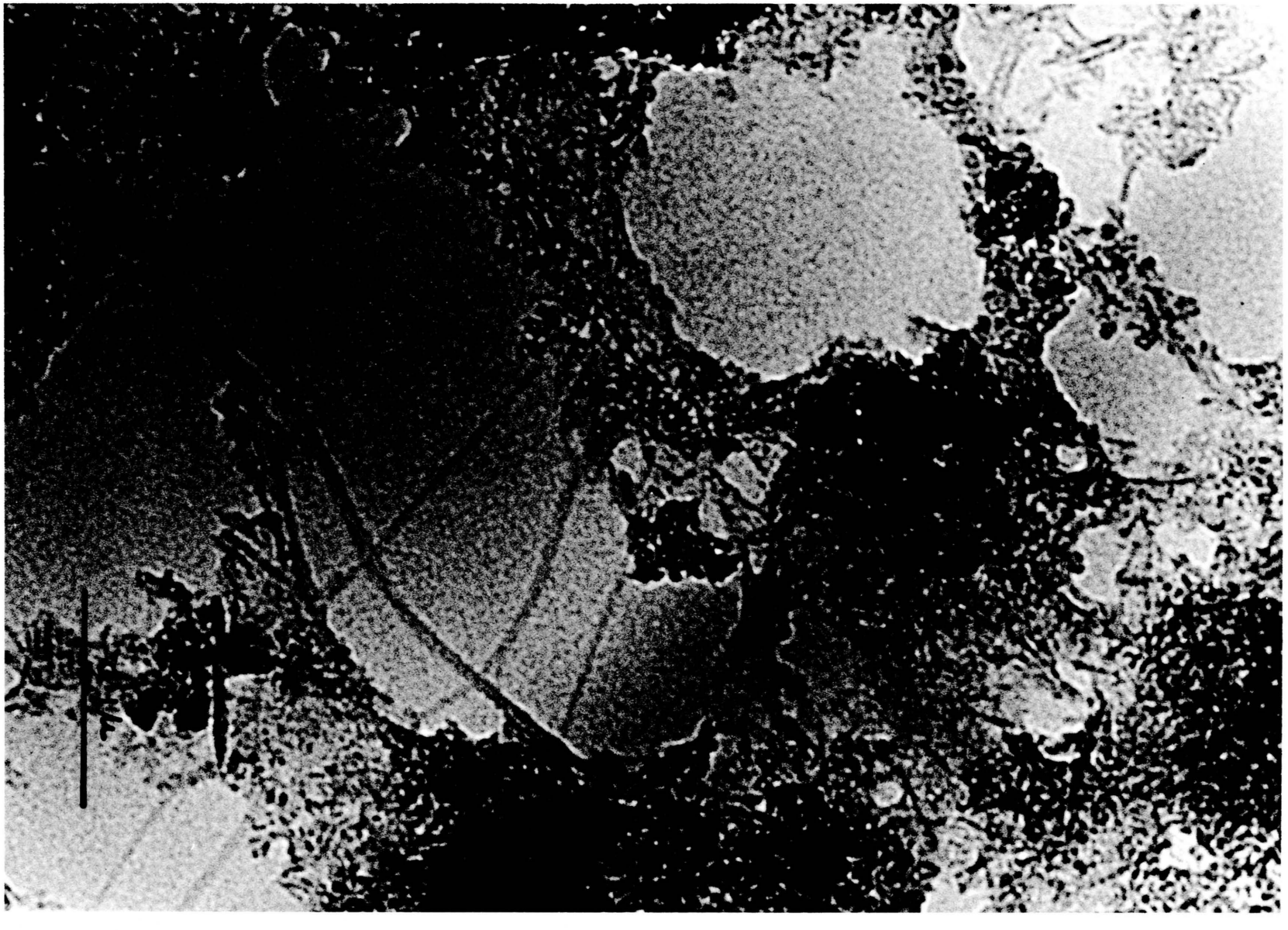


PLATE VII

Electron Micrograph at High Magnification Showing Imogolite Strands of Horizon 1 of the Hilo Soil that Measured about 15-20A in Diameter.
(Magnification: X 380,000)



A comparison of electron micrographs between horizons 1 and 7 indicates a higher content of fibrous material in the surface horizon. The abundance of amorphous materials and fibrous particles may be related to the degree of weathering as suggested by Aomine and Miyauchi (1965).

Discrete amorphous silica in the form of electron dense particles with rounded edges and discs were sporadically observed in electron micrographs from the two horizons. These particles are thought to be opaline silica or the vestiges of volcanic glass.

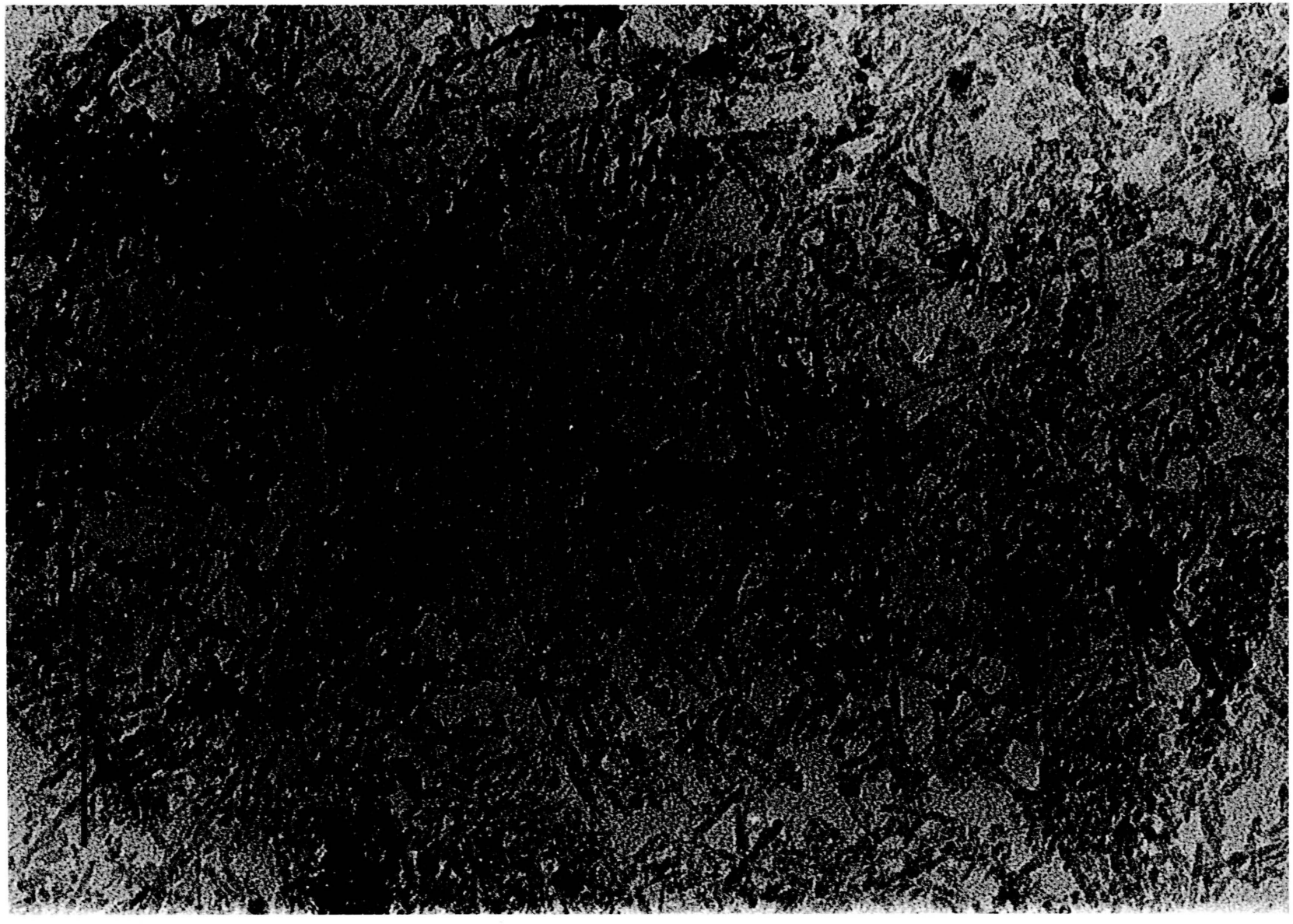
During the final process of removing the excess salts from the soil samples with several washings of distilled water and sonication, it was observed that the supernatant solution was light brown during later washings. Electron micrographs revealed considerable amounts of what might be broken units of imogolite contained in the supernatant solutions (Plate VIII).

Minor Crystalline Components

Poorly formed kaolinite crystals were observed on the electron micrographs in several instances. The presence of mica as confirmed by a Moiré pattern on the crystal surface was also seen occasionally. Broken pieces of feldspar were also present in the two horizons. Viewed at high magnification, iron oxides appeared quite prominent. They appeared to be composed of either very small particles with almost smooth, rounded outlines, or clusters of small particles forming larger irregular aggregates referred to as "black-berries" by Greenland et al. (1968).

PLATE VIII

Electron Micrograph Showing Dispersed Units of Imogolite Suspended in the Light-brown Distilled Water Wash.
(Magnification: X 450,000)



Effects of Treatments

The general effects after chemical treatments could best be evaluated from the influence of organic matter on the quality of electron micrographs and the dissolution effects of the two chemical reagents.

The presence of organic matter appeared to have coagulated the soil into masses of material on the electron microscope substrates. The aggregated masses of opaque materials made scrutiny of the noncrystalline phases difficult. Information to be gained from these micrographs was less than desired.

There were no significant observable effects on electron micrographs of the soils that underwent the two dissolution treatments. The better quality electron micrographs seemed to be related to the absence of organic matter. Better dispersion of the samples was achieved whereby the details of the noncrystalline fractions could be better scrutinized.

Evaluation of the Overall Combined Treatment Effects

1. Chemical Treatments versus X-Ray Diffraction Analysis

The chemical treatments could be divided into pretreatments concerning the oxidation of organic matter using hydrogen peroxide and the differential dissolution techniques to remove the noncrystalline fraction of the soil.

The removal of organic matter has facilitated the dissolution of silicon, iron and aluminum for both of the chemical dissolution reagents discussed earlier. Organic matter-free clay samples resulted in improved x-ray patterns by the appearance of intense peaks and the disappearance of the amorphous band. On the contrary, untreated

samples had less silicon, iron and aluminum removed from the non-crystalline fraction and remnants of the amorphous band still occurred in the x-ray diffraction patterns. This might indicate incomplete removal of the noncrystalline fraction due to its possible stabilization by the humus fractions or the formation of poorly soluble organo-mineral complexes.

2. Chemical Treatments versus Electron Microscopy

If chemical dissolution had been effective in removing the non-crystalline fractions, more features of the crystalline materials could have been detected by electron microscopy.

The removal of organic matter would assist in better clay dispersion so that the morphological characteristics of the noncrystalline materials could be better studied under high magnifications. The effectiveness of Tweneboah method of dissolving some portion of the non-crystalline fraction has allowed better recognition of imogolite, gels, and thickened fibrous constituents.

3. X-Ray Diffraction Analysis versus Electron Microscopy

There seems to be related effects between the x-ray diffractograms of peroxide-treated and untreated clay samples that have undergone the two different dissolution techniques. Organic matter-free residues produced the sharpest electron micrographs and proved to be the most crystalline by x-ray diffraction. The x-ray diffraction patterns of clay residues with organic matter that underwent chemical dissolution gave patterns still with remnants of the amorphous bands. These results were reflected in electron micrographs which showed dense, irregular, opaque materials in which the details were hardly discernible. The

flocculating behavior of clays with organic matter seemed to be common in all sample treated with the chemical dissolution reagents and made it not ideal for electron transmission work.

SUMMARY AND CONCLUSION

The noncrystalline components of the Hilo soil were studied before and after selective acid dissolution utilizing the method of Tweneboah et al. (1967) and 0.5M acetic acid at predetermined pH levels. Both dissolution techniques did solubilize some portion of the noncrystalline components of peroxide-treated and untreated soil samples. The method of Tweneboah was by far the more effective method in removing the noncrystalline components of peroxide-treated soils as substantiated by x-ray analysis.

X-ray diffraction analysis of the clay specimens before and after differential dissolution treatments provided an indirect measure of the effectiveness of each dissolution technique as well as the minerals present in the sample.

Chemical analysis supplemented with x-ray diffraction patterns may not be the ideal way of approximating the efficiency of a dissolution method when applied on a highly amorphous soil. Electron micrographs still showed the presence of residual forms of resistant noncrystalline fraction after the peroxide-treated soil sample from horizons 1 and 7 had undergone the Tweneboah method.

The method of Tweneboah et al. may be effective in removing the "gel-hull" from soils not dominated by amorphous materials. However, the same technique may not be suitable for a highly amorphcus soil like the Hilo soil (Typic Hydrandepts).

The morphology of the soil as revealed by electron micrographs were dominated by imogolite, variable amounts of short fibrous materials,

translucent gels and minor amounts of gibbsite, quartz, feldspar, micas, goethite, magnetite and kaolinite (the presence of which some were confirmed by x-ray diffractograms).

Perhaps, the technique of Tweneboah may be tested to determine its efficiency in removing the noncrystalline components of highly amorphous soils by using higher solution/soil ratios at the two initial extraction levels.

The morphology of the noncrystalline fractions found in this study may strictly apply to volcanic ash soils where intense, humid weathering conditions prevail. Perhaps, studies of amorphous soil of Hawaii from other climatic regimes may provide more information on the chemical effectiveness of the Tweneboah et al. dissolution treatment.

LITERATURE CITED

Aomine, S., and Miyauchi, N. 1965. Imogolite of imogo-layers in Kyushu. Soil Sci. and Plant Nutrition. 5:28-35.

Beutelspacher, H., and van der Marel, H. W. 1968. Atlas of electron microscopy of clay minerals and their admixtures. Elsevier Publishing Company. New York.

Birrell, K. S., and Fieldes, M. 1952. Allophane in volcanic ash soils. J. Soil Sci. 3:156-166.

Cline, M. G. 1955. Soil Survey of the Territory of Hawaii. U.S.D.A. Soil Survey Series, 1939.

Correns, C. W. 1949. Einfuhrung in die mineralogie. Springer-Verlag, Berlin.

Correns, C. W. 1969. Introduction to Mineralogy. Springer-Verlag New York Inc.

Douglas, L. A., and Fiessinger, F. 1971. Degradation of clay minerals by H_2O_2 treatments to oxidize organic matter. Clays and Clay Minerals. Pergamon Press. London. 19:67-68.

Egawa, T. 1964. Mineralogical properties of volcanic ash soils in Japan. F.A.O. World Soil Resources Rpt. 14:89-91.

Farmer, V. C., and Mitchell, B. D. 1963. The occurrence of oxalates in soil clays following hydrogen peroxide treatment. Soil Sci. 96:221-229.

Follett, E. A. C., McHardy, W. J., Mitchell, B. D., and Smith, B. F. L. 1965. Chemical dissolution techniques in the study of soil clays. Part I. Clay Minerals Bull. 5:128-144.

Fox, R. L., DeDatta, S. K., and Sherman, G. D. 1962. Phosphorus solubility and availability to plants and the aluminum status of Hawaiian soils as influenced by liming. Trans. Joint Meeting. Comm. IV and V, Int. Soc. of Soil Sci., N. Z. pp. 574-583.

Fox, R. L., Hasan, S. M., and Jones, R. C. 1971. Phosphate and sulphate adsorption by latosols. Proc. of the Int. Symposium on Soil Fertility Evaluation, New Delhi. 1:857-864.

Greenland, D. J., Oades, J. M., and Sherwin, T. W. 1968. Electron microscope observations of iron oxides in some red soils. J. of Soil Sci. 19:119-126.

Hashimoto, I., and Jackson, M. L. 1960. Rapid dissolution of allophane and kaolinite-halloysite after dehydration. Clays and Clay Minerals, 7th Conf., Pergamon Press, London. pp. 102-113.

Hsu, Pa Ho. 1963. Effect of initial pH, phosphate and silicate on the determination of aluminum and aluminon. Soil Sci. 96:230-238.

Jackson, M. L. 1958. Soil Chemical Analysis. Prentice Hall, Englewood Cliffs. N. J.

Jackson, M. L. 1964. Free oxides, hydroxides, and amorphous aluminosilicates. Methods of Soil Analysis, Agronomy Monograph, No. 9. American Society of Agronomy, Madison, Wisconsin.

Jackson, M. L. 1956. Soil Chemical Analysis -- Advanced Course. Published by the author, Madison, Wisconsin.

Jones, R. C. 1963. An Electronmicroscopic Examination of Arizona Bentonite. M.S. Thesis, Univ. of Arizona, Tucson.

Jones, R. C., and Uehara, G. 1972. Amorphous Coatings on Mineral Surfaces. Soil Sci. Soc. of Amer. Proc. (in Press).

Jones, R. C. 1972. Personal Communication. Univ. of Hawaii, Honolulu.

Jones, L. H. P., and Handreck, K. A. 1963. Effects of iron and aluminum oxides on silica in solution in soils. Nature. 198:852-853.

Kanehiro, Y., and Chang, A. 1956. Cation Exchange Properties of the Hawaiian Great Soil Groups. Hawaii Agr. Expt. Sta. Tech. Bull. 31:5-27.

Kanehiro, Y., and Sherman, G. D. 1956. Effect of dehydration-rehydration on cation exchange capacity of Hawaiian soil. Soil Sci. Soc. of Amer. Proc. 20:341-344.

Kanehiro, Y., and Whittig, L. D. 1961. Amorphous mineral colloids of soils of the Pacific region and adjacent areas. Pacific Science. 40:477-482.

Kawasaki, H., and Aomine, S. 1965. So-called 14A clay minerals in some ando soils. Soil Sci. and Plant Nutrition. 12:144-151.

Lai, S. H., and Swindale, L. D. 1967. Chemical properties of allophane from Hawaiian and Japanese soils. Soil Sci. Soc. Amer. Proc. 33:804-808.

Loughnan, F. C. 1969. Chemical Weathering of the Silicate Minerals. American Elsevier Publishing Company, Inc. New York.

McKeague, J. A., and Cline, M. G. 1963. Silica in soils. Advances in Agronomy. 15:339-396.

Mitchell, B. D., and Mackenzie, R. C. 1954. Removal of free iron oxide from clays. Soil Sci. 77:173-184.

Mitchell, B. D., and Farmer, V. C. 1962. Amorphous clay minerals in some Scottish soil profiles. Clay Minerals Bull. 5:128-144.

Mitchell, B. D., Farmer, V. C., and McHardy, W. J. 1964. Amorphous inorganic materials in soils. Advances in Agronomy. 16:327-375.

Miyauchi, N., and Aomine, S. 1966. Mineralogy of gel-like substance in the pumice bed in Kanuma and Kitakami districts. Soil Sci. and Plant Nutrition. 13:19-22.

Moberly, R. 1963. Amorphous marine muds from tropically weathered basalt. Amer. J. of Sci. 261:767-772.

Morey, G. W., Fournier, R. O., and Rowe, J. J. 1964. The solubility of amorphous silica at 25°C. J. Geophys. Res. 69:1995-2002.

Oades, J. M., and Townsend, W. N. 1963. The influence of iron on the stability of soil organic matter during peroxidation. J. of Soil Sci. 14:134-143.

Olphan, H. van. 1971. Amorphous clay minerals. Science. 171:90-91.

Olson, R. V. 1964. Total iron. Methods of Soil Analysis, Agronomy Monograph No. 9, American Society of Agronomy, Madison, Wisconsin.

Ostrom, M. E. 1961. Separation of clay minerals from carbonate rocks using acid. J. Sediment. Petrol. 31:123-129.

Rich, C. I., and Thomas, G. W. 1960. The clay fractions of soils. Advances in Agronomy. 12:1-34.

Rixon, A. J. 1966. Effects of heavy application of lime to soils derived from volcanic ash on the humid Hilo and Hamakua coast, island of Hawaii. Hawaii Agr. Expt. Sta. Tech. Bull. 47:3-54.

Ross, C. S., and Kerr, P. F. 1934. Halloysite and allophane. U. S. Geol. Survey, Prof. Paper. 185:135-148.

Russell, E. W. 1961. Soil Conditions and Plant Growth. 9th ed. John Wiley and Sons, Inc. New York.

Russell, J. D., McHardy, W. J., and Fraser, A. R. 1969. Imogolite: A Unique Aluminosilicate. Clay Minerals. 8:87-99.

Schwertmann, U. 1959. Z. Pflanzenernaehr Dueng. Bodenk 84:194-204.

Sherman, G. D. 1962. Weathering and soil science. Trans. of Joint Meeting of Comm. IV and V of Int. Soc. of Soil Sci. - Lower Hutt, N. Z. pp. 24-32.

Sherman, G. D., Matsusaka, Y., Ikawa, H., and Uehara, G. 1964. The role of the amorphous fraction in the properties of tropical soils. Agrochimica (Rome). 8:146-163.

Sherman, G. D., Walker, J. L., and Ikawa, H. 1968. Some of the mineral resources of the Hawaiian Islands.

Sudo, T. 1954. Clay mineralogical aspects of the alteration of volcanic glass in Japan. Clay Minerals Bull. 2:96-106.

Swindale, L. D. 1964. The properties of soils developed from volcanic ash. F.A.O. World Soils Rpt. 14, Rome.

Tamura, T., Jackson, M. L., and Sherman, G. D. 1953. Mineral content of low humic and hydrol humic latosols of Hawaii. Soil Sci. Soc. Amer. Proc. 17:343-346.

Tenma, H. H. 1965. Some characteristics of noncrystalline constituents in Hawaiian soils. M.S. Thesis, Univ. of Hawaii, Honolulu.

Tokudome, S., and Kanno, I. 1965. Nature of the humus of humic allophane soils in Japan. Soil Sci. and Plant Nutrition. 11:185-192.

Tweneboah, C. K., Greenland, D. J., and Oades, J. M. 1967. Changes in the charge characteristics of soils after treatment with 0.5M Calcium Chloride at pH 1.5. Australian J. Soil Res. 5:247-261.

Voss, R. L. 1970. The characteristics and genesis of the Akaka and Hilo soils on the island of Hawaii. M.S. Thesis, Univ. of Hawaii, Honolulu.

Wada, K. 1967. A structural scheme of soil allophane. The Amer. Mineralogist. 52:691-708.

Yoshinaga, N., and Aomine, S. 1962. Allophane in some ando soils. Soil Sci. and Plant Nutrition. 8:6-13.

Yoshinaga, N. 1966. Chemical composition and some thermal data of eighteen allophanes from ando soils and weathered pumices. Soil Sci. and Plant Nutrition. 12:47-54.

Yoshinaga, N., Wada, K., Yotsumoto, H., Ibe, K., and Aida, S. 1970. High resolution electron micrographs of imogolite. Clay Minerals. 8:487-489.